

# JOURNAL OF THE CHEMICAL SOCIETY.

## ABSTRACTS OF PAPERS ON ORGANIC CHEMISTRY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
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### PART I.

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#### Organic Chemistry.

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**Bromination with Aluminium Bromide in the Aliphatic Series.** By A. MOUNEYRAT (*Compt. rend.*, 1898, 127, 109—111. Compare Abstr., 1898, i, 613).—Aluminium bromide behaves as a powerful brominating agent, because, like aluminium chloride, it has the property of producing double linkings in alkylic haloids. When it is heated with dry ethylenic dibromide, hydrogen bromide and acetylene are obtained, and if bromine is also present, this combines additively with the unsaturated compound thus produced. The author shows that, by means of aluminium bromide, ethylic bromide can be successively converted into ethylenic dibromide, acetylene tetrabromide, and hexabromethane. By this method, hexabromethane is most readily prepared from acetylene tetrabromide, the yield obtained being 65—70 per cent. G. T. M.

**Action of Chloroform on Aqueous Alkali.** By JOHANNES THIELE and FRANKLAND DENT (*Annalen*, 1898, 302, 273—274. Compare Desgrez, Abstr., 1898, i, 166).—Geuther has observed that chloroform yields carbonic oxide with aqueous and alcoholic alkalis (*Annalen*, 1862, 123, 121); under conditions described by the authors, it is found that quantities of chloroform varying between 21 per cent. and 66 per cent. are convertible into formic acid through the action of caustic soda. M. O. F.

**Decomposition of Iodoform Solutions.** By J. BOUGAULT (*J. Pharm.*, 1898, [vi], 8, 213—214).—On exposing a sealed glass vessel containing a solution of iodoform in ether together with mercury or centinormal aqueous sodium thiosulphate to bright sunlight, iodine is initially liberated in the ethereal layer; on shaking,

however, the iodine is removed, but on further exposure more sodium is set free, which can be removed as before. Ultimately, however, no more iodine is liberated, even on long exposure to light; from this it is concluded that light alone does not affect iodoform, but that its decomposition is due to oxidation. This view is confirmed by the presence of a considerable quantity of formic acid in an ethereal solution of iodoform from which iodine has separated. W. A. D.

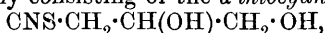
**Composition and Solubility of Sodium Ferrocyanide.** By JAMES T. CONROY (*J. Soc. Chem. Ind.*, 1898, 17, 103—106).—Analyses of several specimens of pure sodium ferrocyanide show that it contains  $10\text{H}_2\text{O}$ . Its solubility at various temperatures was determined by means of a special form of apparatus; an excess of the salt was agitated by means of a current of air with water contained in a large test-tube surrounded by water at a known temperature. The test-tube was connected by a glass-tube with a weighing bottle completely immersed in the water of the heating bath, so that by suction at a second tube with which the weighing bottle was provided, the saturated solution of the salt could be transferred to the latter; by determining the weight of the solution thus transferred, and the quantity of salt it left on evaporation, the solubility was ascertained. The tube connecting the dissolving tube with the weighing bottle was provided with a filtering plug by which the liquid transferred could be freed from undissolved material. Curves are given which show the solubility in water of sodium and potassium ferrocyanides at temperatures between  $15^\circ$  and  $100^\circ$ ; it appears that, whereas the solubility of anhydrous potassium ferrocyanide is always greater than that of the anhydrous sodium salt, hydrated potassium ferrocyanide,  $\text{K}_4\text{FeC}_6\text{N}_6 + 3\text{H}_2\text{O}$ , is more soluble than the sodium salt,  $\text{Na}_4\text{FeC}_6\text{N}_6 + 10\text{H}_2\text{O}$ , only at temperatures below  $54^\circ$ .

On adding 50 grams of crystalline sodium ferrocyanide dissolved in water (50 c.c.) to a solution of 60 grams of potassium carbonate in 60 c.c. of water, 93 per cent. of the potassium ferrocyanide theoretically possible separates on standing. When a solution of 50 grams of sodium carbonate in 150 c.c. of water is added to 50 grams of potassium ferrocyanide dissolved in 100 c.c. of water, no crystals separate on standing, but on evaporating the liquid to one-half its volume, sodium and potassium ferrocyanide crystallise together. When, however, an aqueous solution of 60 grams of sodium chloride and 50 grams of potassium ferrocyanide is allowed to crystallise, 91 per cent. of the sodium ferrocyanide theoretically possible is obtained; on the other hand, a solution of 60 grams of potassium chloride and 50 grams of sodium ferrocyanide deposits 60 per cent. of the theoretical quantity of potassium ferrocyanide. These phenomena are elucidated by the values given of the solubility of potassium and sodium ferrocyanide in solutions of the alkali chlorides and carbonates; at ordinary temperatures, potassium ferrocyanide is very slightly soluble in saturated aqueous potassium chloride, and sodium ferrocyanide in sodium chloride solution. Similarly, each ferrocyanide is very sparingly soluble in a solution of the carbonate of its own metal.

W. A. D.

### Action of Metallic Thiocyanates on Aliphatic Chlorhydrins.

By WILBER D. ENGLE (*J. Amer. Chem. Soc.*, 1898, 20, 668—678).—On heating  $\alpha$ -chloropropylene glycol,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$  (14 grams), dissolved in 95 per cent. alcohol, with potassium thiocyanate (13 grams) during 4 days on the water-bath, potassium chloride gradually separates; on removing the latter, and again heating, a white, resinous *substance* separates, which is insoluble in all organic solvents, and gives none of the reactions of organic thiocyanates. It contains C = 40.145; H = 5.168; N = 7.560; S = 27.281, and O = 19.846 per cent.; it is not affected by hydrochloric or sulphuric acid, and by aqueous ammonia or potash, but is decomposed by bromine, giving a tarry product, and is oxidised by concentrated nitric acid to sulphuric and oxalic acids. A small amount of an oil having a garlic-like odour, and apparently consisting of the  $\alpha$ -thiocyanhydrin,



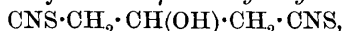
is formed along with the white substance above described, but on attempting to purify it, it is immediately converted into the latter. The same products are obtained, in similar proportion, by heating  $\alpha$ -chloropropylene glycol with potassium thiocyanate in sealed tubes at 110—115°; at 120°, however, there is a considerable amount of decomposition.

When an alcoholic solution of  $\alpha\beta$ -dibromopropyl alcohol (40 grams) is heated with potassium thiocyanate (37 grams) during 6 days, potassium bromide separates, and on removing the alcohol by evaporation, washing with water, and extracting with ether, 10 c.c. of a dark coloured oil is obtained, which appears to consist principally of the *dithiocyanhydrin*,  $\text{CNS}\cdot\text{CH}_2\cdot\text{CH}(\text{CNS})\cdot\text{CH}_2\cdot\text{OH}$ ; it cannot be purified by distillation as it immediately resinifies, but its identity is established by its yielding *imidomethanepropyl alcohol bisulphide*

*hydrochloride*,  $\text{OH}\cdot\text{CH}_2\cdot\underset{\text{CH}_2\cdot\text{S}}{\overset{\text{CH}-\text{S}}{\text{C}}}\cdot\text{NH}\cdot\text{HCl}$ , when reduced by means

of tin and hydrochloric acid; this separates from alcohol in transparent, colourless, tetragonal crystals, whilst its *tin* double salt forms large octahedra. The dithiocyanhydrin described can be more rapidly prepared by heating the mixture mentioned above for 8 hours at 110—115°; at higher temperatures, decomposition occurs, and in all cases a considerable amount of a resinous *substance*, similar to that obtained from  $\alpha$ -chloropropylene glycol, is formed. The  $\alpha$ -acetyldithiocyanhydrin, obtained by heating  $\alpha\beta$ -dibromopropyl acetate (17 grams) with potassium thiocyanate (13 grams) and alcohol (10 c.c.) for 4 hours at 120°, is a red oil which cannot be distilled.

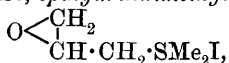
Only a small quantity of the  $\alpha\gamma$ -dithiocyanhydrin,



is formed when  $\alpha\gamma$ -dichlorisopropyl alcohol is heated with alcoholic potassium thiocyanate, either on the water bath during 4 days, or in a sealed tube for 2 hours at 175°; the principal product in each case is a yellow, sponge-like *resin*. A similar *substance* is obtained from  $\alpha\gamma$ -dichlorisopropyl acetate under the same conditions.

Potassium thiocyanate readily interacts with epichlorhydrin and

epibromhydrin at 40—50°, a good yield of the corresponding *epithiocyanhydrin*,  $\text{CNS} \cdot \text{CH}_2 \cdot \underset{\text{CH}_2}{\text{CH}} > \text{O}$ , being obtained; when freed from potassium thiocyanate by washing with water, and from condensation products by dissolving in ether, the cyanhydrin is obtained as a transparent, dark red liquid with an odour of garlic. It cannot be distilled, and closely resembles the cyanhydrins already described; when treated with hydrogen sulphide under a pressure of 960 mm., it does not yield a derivative of carbamic acid, but a thick, syrupy liquid, probably a sulphide. On heating epithiocyanhydrin with an excess of methylic iodide at 100° for 6 hours, *epihydrindimethylsulphine iodide*,



is formed; it crystallises from water in monosymmetric plates, and decomposes at 195—200° without melting. W. A. D.

**Betaine contained in the Root of *Althæa Officinalis*.** By N. A. ORLOFF (*Chem. Centr.*, 1898, i, 37; from *Pharm. Zeit. Russ.*, 36, 631—632).—Betaine can be obtained from the aqueous extract of the root of *Althæa officinalis* after removing the asparagine by precipitating it with nitric acid and sodium phosphomolybdate; the free base obtained by treating the precipitate with barium hydroxide forms colourless crystals, is soluble in water and alcohol, and insoluble in ether. The hydrochloride is easily crystallised, and does not change on exposure to the air. With potassium dichromate solution and hydrochloric acid, betaine does not exhibit any colour reaction. It is precipitated by picric acid, zinc chloride, and auric chloride, but not by tannin; the aurochloride,  $\text{C}_5\text{H}_{11}\text{NO}_2 \cdot \text{HAuCl}_4$ , crystallises in microscopic plates, or in short crystals arranged in the form of a cross. E. W. W.

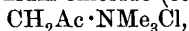
**Ketonic Bases.** By ERNST SCHMIDT (*Arch. Pharm.*, 1898, 236, 334—343. Compare following abstract).—The following compounds containing ketonic groups, which have been prepared by the action of trimethylamine or pyridine on monochloracetone and bromacetophenone, namely, *trimethylacetonylammonium chloride*, *pyridylacetonyl chloride*, *trimethylacetophenylammonium bromide*, and *pyridylacetophenyl bromide*, readily yield oximes on treatment with hydroxylamine. The reagents usually employed for producing the Beckmann rearrangement do not act on these oximes in the usual manner; phosphorus pentachloride alone appears to produce the rearrangement, but owing to the instability of the bases formed, it could not be definitely decided whether this is the case or not. The oximes of trimethylacetophenylammonium bromide and pyridylacetophenyl bromide are converted by boiling with acetic chloride into monacetyl derivatives, whereas in closed vessels this reagent has no action on them.

A detailed account of the physiological action of these ketonic bases and their oximes is given.

The action of primary, secondary, and other tertiary bases on monochloracetone and bromacetophenone has been studied, and the following

additive products prepared. *Quinolyl-* and *isoquinolyl-acetonyl chloride* compounds from quinoline, strychnine, and hydrastine with brom-acetophenone; *acetonylpiperidine hydrochloride*; *acetonylmethylpyridine chloride*; *acetophenylpiperidine hydrobromide*; *diacetophenylpiperidine bromide*; *dimethylacetophenylammonium bromide*; *dimethyldiacetophenylammonium bromide*; *methylacetophenylammonium bromide*; *methyldiacetophenylammonium bromide*, and possibly *methyltriacetophenylammonium bromide*.  
A. W. C.

**Trimethylacetonylammonium Chloride.** By A. L. C. FURNÉE (*Arch. Pharm.*, 1898, **236**, 343—353. Compare preceding abstract).—Trimethylacetonylammonium chloride (coprine chloride),



first prepared by Niemilowicz (*Monatsh.*, 1886, **7**, 242) by the interaction of monochloroacetone and trimethylamine, is a crystalline substance. The *platinochloride* forms yellowish-red needles melting at 238—240°; the *aurochloride* crystallises in beautiful, yellow needles melting at 139·5°. The *oxime* separates from a mixture of alcohol and ethylic acetate in colourless plates melting at 212°, and is readily soluble in water and alcohol, but almost insoluble in cold ether and ethylic acetate; it yields an *aurochloride* crystallising in fine yellow needles melting at 170—171°, and a *platinochloride* in yellowish-red crystals melting at 206°.

When reduced with sodium amalgam, the *oxime* is reconverted into trimethylacetonylammonium chloride; only on one occasion was a substance obtained which, from analysis of its *aurochloride*, melting at 156°, and its *platinochloride*, melting at 210°, appeared to be the desired amine.

Attempts to bring about the Beckmann rearrangement led to the following results. The *oxime* is not altered by heating with 25 per cent. hydrochloric acid; or by concentrated sulphuric acid or acetic chloride at 100° in sealed tubes. Trimethylacetonylammonium chloride is re-formed when the *oxime* is treated with concentrated hydrochloric acid either at 0° or when heated with it in sealed tubes at 150°; and on heating with concentrated sulphuric acid at 100° for 10 minutes.

When boiled with acetic chloride or acetic anhydride, an *acetyl* derivative is obtained as a radiating, crystalline mass, giving a beautiful, yellow crystalline *aurochloride* melting at 120°. On boiling with benzoic chloride, a *benzoyl* derivative is obtained; its *aurochloride* forms yellow crystals melting at 165°, whilst the *platinochloride* melts at 212°.

When the *oxime* is dissolved in phosphorus oxychloride and phosphorus pentachloride slowly added, rearrangement takes place, a reaction which is being further studied. The product gives an *aurochloride* crystallising from water in star-shaped groups of needles melting at 128°, and a *platinochloride* separating in needles and melting at 227°.

A. W. C.

**Free Chitosamine.** By CORNELIS A. LOBRY DE BRUYN (*Ber.*, 1898, **31**, 2476—2477).—In connection with Breuer's recent note on free chitosamine (*Abstr.*, 1898, **i**, 620), the author draws attention to

the fact that the base had already been isolated (L. de Bruyn and Alberda van Ekenstein, *Kong. Akad. Wiss. Amsterdam*, January 2, 1897), and gives an extract from the published note.

The base was isolated by acting on the powdered hydrochloride with sodium methoxide dissolved in methylic alcohol, and was obtained in the form of needles by precipitation with dry ether. It is very hygroscopic, and dissolves readily in water. When its solution in methylic alcohol is kept, it furnishes a crystalline substance which is identical with that obtained by acting with ammonia on a solution of fructose in methylic alcohol. It follows that the sugar from which chitosamine is derived is related to fructose.

Chitosamine hydrochloride, when treated with silver carbonate, yields a substance which gives glucosazone with phenylhydrazine, and a well-crystallised polyacetate on treatment with acetic chloride.

A. L.

**Compounds of Hexamethylenetetramine (Urotropine).** By BRUNO GRÜTZNER (*Arch. Pharm.*, 1898, **236**, 370—381).—Hexamethylenetetramine has been obtained by Butlerow by passing ammonia over methylene oxide, and is now used as a medicine under the name of urotropine. The author prepared the substance according to Hofmann's directions, by evaporating a solution of formaldehyde with excess of ammonia; during the process, it was observed that, on warming a cold saturated aqueous solution of the base, a precipitate is formed, which disappears again on cooling; this is possibly due to the formation of a compound with water.

The following compounds of hexamethylenetetramine have been prepared. The *hydrobromide*, slender white needles, very soluble in water; the *hydriodide*, which is decomposed by water, with separation of iodine; the *arsenate*,  $C_6H_{12}N_4 \cdot H_3AsO_4 + \frac{1}{2}H_2O$ , glistening, silken crystals; *hexamethyleneamine silver nitrate*,  $C_6H_{12}N_4 \cdot AgNO_3$ , microscopic, rhombic plates, soluble in water with a neutral reaction; by the action of silver nitrate on hexamethyleneamine in molecular proportion in presence of nitric acid, a mixture of the compound,  $C_6H_{12}N_4 \cdot AgNO_3 \cdot HNO_3$ , and the above substance is obtained as a microcrystalline precipitate; *hexamethyleneamine mercuric chloride*,  $C_6H_{12}N_4(HgCl_2)_2$ , white needles, which, when powdered, are strongly electric; the *compound*  $C_6H_{12}N_4 \cdot HgCl_2$ , obtained as a crystalline precipitate, by adding mercuric chloride (1 mol.) to an alcoholic solution of the base (1 mol.); *hexamethyleneamine hydrochloride mercuric chloride*,  $(C_6H_{12}N_4 \cdot HCl)_2(HgCl_2)_3$ , a voluminous precipitate of microscopic, flat, monoclinic plates; *hexamethyleneamine mercuric iodide*,  $C_6H_{12}N_4 \cdot HgI_2$ , white, glistening needles; *hexamethyleneamine mercuric cyanide*, crystalline precipitate of hexagonal pyramids, readily soluble in water and alcohol; *hexamethyleneamine magnesium chloride*,  $(C_6H_{12}N_4)_2 \cdot MgCl_2 + 9H_2O$ , triclinic prisms soluble in water with a faintly alkaline reaction; *hexamethyleneamine hydrochloride zinc chloride*,  $C_6H_{12}N_4 \cdot HCl \cdot ZnCl_2$ , groups of needle-shaped crystals; and *hexamethyleneamine hydrochloride cadmium chloride*,  $C_6H_{12}N_4 \cdot HCl \cdot CdCl_2 + H_2O$ , monoclinic prisms almost insoluble in cold water.

Bismuth, antimony, and zinc chlorides give crystalline precipitates



with the base in hydrochloric acid solution, which are at once decomposed by water with formation of basic salts. A. W. C.

**Silver Derivative of Guanidine.** By JOHANNES THIELE (*Annalen*, 1898, 302, 334).—The *silver* derivative,  $\text{CH}_3\text{N}_3\text{Ag}_2$ , is obtained as a white, flocculent precipitate, containing  $1\text{H}_2\text{O}$ , when baryta is added to a mixture of guanidine and silver nitrates in molecular proportion.

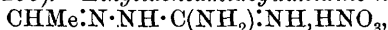
M. O. F.

**Preparation of Amidoguanidine.** By JOHANNES THIELE (*Annalen*, 1898, 302, 332—334. Compare Abstr., 1892, 1296).—Moderately dilute solutions of amidoguanidine salts, when treated with sodium hydrogen or potassium hydrogen carbonate, yield *amidoguanidine hydrogen carbonate*,  $\text{NH}_2\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{H}_2\text{CO}_3$ , which is practically insoluble in cold water, and melts and decomposes at  $172^\circ$ ; boiling water dissolves it in part, but also eliminates carbonic anhydride and ammonia. Although caustic alkalis remove carbonic anhydride, ammonia is without action on the substance, which is also formed when ammonium carbonate is added to an amidoguanidine salt, ammonia being eliminated.

In view of the fact that guanidine salts do not yield a precipitate with alkali hydrogen carbonates, the formation of a sparingly soluble salt with amidoguanidine may be utilised in the preparation of this compound.

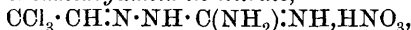
M. O. F.

**Condensation of Amidoguanidine with Aliphatic Aldehydes and Ketones.** By JOHANNES THIELE and EDUARD DRALLE (*Annalen*, 1898, 302, 275—299).—*Ethylideneamidoguanidine nitrate*,



separates in small prisms when a solution of amidoguanidine nitrate is treated with aldehyde, and allowed to evaporate over sulphuric acid; it melts at  $144^\circ$ , and gradually reduces ammoniacal silver nitrate. The hydrochloride and the free base are very unstable, and have not been isolated.

*Trichlorethylideneamidoguanidine nitrate*,

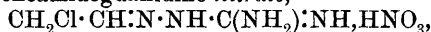


crystallises in prisms containing  $1\text{H}_2\text{O}$ ; it melts and decomposes at  $113^\circ$ , and yields amidoguanidineglyoxylic acid when the aqueous solution is boiled. The *hydrochloride* forms beautiful plates containing  $2\text{H}_2\text{O}$ ; it melts at  $83\text{--}84^\circ$ , and decomposes at  $110^\circ$ .

*Amidoguanidineglyoxylic acid*,  $\text{NH:C}(\text{NH}_2)\cdot\text{NH:N}\cdot\text{CH}\cdot\text{COOH}$ , produced in the manner indicated, contains  $1\text{H}_2\text{O}$ , and melts and decomposes at  $150\text{--}157^\circ$ , according to the rate at which it is heated; the *hydrochloride* and *nitrate*, each containing  $1\text{H}_2\text{O}$ , melt and decompose at  $197^\circ$  and  $182^\circ$  respectively, whilst the *sulphate* crystallises in silky leaflets melting and decomposing at  $136\text{--}137^\circ$ . The *calcium*, *barium*, and *silver* salts each contain  $1\text{H}_2\text{O}$ , and the *methylic* salt, which melts and decomposes at  $187\text{--}188^\circ$ , forms a *hydrochloride* which contains  $\frac{1}{2}\text{H}_2\text{O}$ , and melts at  $106\text{--}108^\circ$ ; in the anhydrous condition, the last-named substance melts at  $110^\circ$ , and decomposes at  $160^\circ$ . Reduction with tin and hydrochloric acid converts amidoguanidineglyoxylic acid into the *base*,  $\text{C}_3\text{N}_4\text{H}_6\text{O}$ , which forms a sparingly soluble *nitrate* melting at  $308^\circ$ .

*Glyoxalbisamidoguanidine*,  $C_2H_2[:N \cdot NH \cdot C(NH_2) : NH]_2$ , is sparingly soluble in cold water, forming a yellow, alkaline solution in hot water; it crystallises in elongated, yellowish leaflets containing  $1H_2O$ , which melt and decompose at  $265-266^\circ$ . The *nitrate* is prepared by boiling an aqueous solution of amidoguanidine hydrochloride with excess of dichloraldehyde, and treating the liquid with nitric acid; it crystallises in white leaflets, and melts and decomposes at  $292^\circ$ . The *hydrochloride* forms long needles melting at  $277^\circ$ , and the *platinochloride*, which is sparingly soluble in water, crystallises in golden yellow needles; the *sulphate* contains  $4H_2O$  and melts at  $280-281^\circ$ ; the *dichromate* forms red, microscopic prisms, and the *nitrite* melts at  $211^\circ$ .

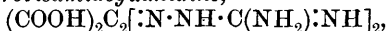
*Chlorethylideneamidoguanidine nitrate*,



forms crystals resembling ammonium chloride, and melts and decomposes at  $144^\circ$ ; glyoxalbisamidoguanidine nitrate is produced on boiling the aqueous solution.

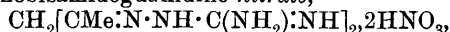
*Diacetylbisamidoguanidine*,  $C_2Me_2[:N \cdot NH \cdot C(NH_2) : NH]_2$ , forming small, yellow crystals, melts and decomposes at  $248-249^\circ$ ; the *hydrochloride* crystallises in long needles containing  $2H_2O$ , and melts at  $308^\circ$ . The *nitrate* becomes brown at  $240^\circ$ , without undergoing fusion, and the *platinochloride* forms needles containing  $2H_2O$ .

*Dihydroxytartarobisamidoguanidine*,



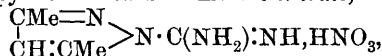
prepared from amidoguanidine hydrochloride and sodium dihydroxytartrate, is a white precipitate which contains  $2H_2O$ , and resembles starch; it becomes brown at  $230^\circ$ , but does not melt. The *hydrochloride* contains  $2H_2O$ , and melts and decomposes at  $235^\circ$ ; the *calcium* salt forms white needles containing  $4H_2O$ , and the *silver* salt contains  $2H_2O$ .

*Acetylacetonebisamidoguanidine nitrate*,



gradually separates in large, rhombic crystals when acetylacetone is added to an aqueous solution of amidoguanidine nitrate (2 mols.); it slowly reduces an ammoniacal solution of silver nitrate, and melts at  $197-199^\circ$ . When the aqueous solution is boiled for several hours, amidoguanidine nitrate is eliminated, and dimethylpyrazolecarbonamide nitrate produced.

*3 : 5-Dimethylpyrazole-1-carbonamide nitrate*,



crystallises from alcohol in white needles which melt and effervesce at  $168^\circ$ ; boiling caustic soda in a reflux apparatus converts it into 3 : 5-dimethylpyrazole, which melts at  $106-107^\circ$ .

*Acetonylacetonebisamidoguanidine*,  $C_2H_4[CHMe : N \cdot NH \cdot C(NH_2) : NH]_2$ , crystallises from water in small, yellow prisms, which melt and effervesce at  $224-225^\circ$ ; the *nitrate* melts at  $239-240^\circ$ , and the *hydrochloride*, which contains  $2H_2O$ , melts at  $256-258^\circ$ . The *platinochloride* forms yellow, microscopic needles, and contains  $2H_2O$ .

The *base*,  $C_7H_{12}N_4$ , is produced when amidoguanidine hydrochloride and acetonylacetone, in molecular proportion, are heated with alcohol

and a little water for  $2\frac{1}{2}$  hours in a reflux apparatus; it melts at  $151^{\circ}$ , and is so stable towards hydrolytic agents as to render it probable that the substance is a cyclic compound. The *hydrochloride* and *nitrate* melt at  $244$ — $245^{\circ}$  and  $188^{\circ}$  respectively. M. O. F.

**Diazoacetoneitrile.** By THEODOR CURTIUS (*Ber.*, 1898, 31, 2489—2492).—When methyleneamidoacetoneitrile is treated with alcoholic normal hydrochloric acid, the salt of amidoacetoneitrile is produced (Jay and Curtius, *Abstr.*, 1894, i, 162), but if a saturated alcoholic solution of hydrogen chloride is used, *glycineamidoether dihydrochloride*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{C}(\text{OEt}) \cdot \text{NH} \cdot 2\text{HCl}$ , is obtained; it is hygroscopic, and melts, evolving gas, at  $170$ — $188^{\circ}$ . Nitrous acid converts it into ethylic diazoacetate.

**Diazoacetoneitrile**,  $\text{N}_2 \cdot \text{CH} \cdot \text{CN}$ , obtained by the action of nitrous acid on amidoacetoneitrile, is a limpid, orange-yellow liquid, having, when freshly prepared, the odour of acetoneitrile, but rapidly becoming pungent; it boils at  $46.5^{\circ}$  under a pressure of  $14$ — $15$  mm., and does not solidify at  $-18^{\circ}$ . It dissolves in water, and is much less stable than ethylic diazoacetate, being also more volatile than this substance in the vapour of ether. It explodes when brought into contact with copper oxide at the ordinary temperature. M. O. F.

**Tetracetylhydrazide and Derivatives of Urazole.** By GEROLAMO CUNEO (*Chem. Centr.*, 1898, i, 38—39; from *Ann. Chim. Farm.*, 1897, 26, 481—490).—By the action of methylic iodide on urazole at  $120^{\circ}$ , *methylurazole* and *dimethylurazole* are obtained; the former crystallises from water in small needles, is insoluble in chloroform, and melts at  $216^{\circ}$ , the latter crystallises from chloroform, in which it is easily soluble, and melts at  $167^{\circ}$ . Attempts to introduce another methyl group failed. *Diacetylurazole* prepared by heating 1 part of urazole with 6 parts of acetic anhydride for half-an-hour, crystallises from alcohol in white leaflets, is insoluble in ether, and melts at  $206^{\circ}$ ; when boiled with water, it yields *acetylurazole*, which crystallises from water in colourless crystals, and melts at  $221.5^{\circ}$ . *Triacetylurazole* is obtained by heating diacetylurazole with 6 times its weight of acetic anhydride for 5 hours, and evaporating the solution in a vacuum over lime; it crystallises from anhydrous benzene in prisms, melts at  $138^{\circ}$ , is decomposed by the prolonged action of boiling acetic anhydride with formation of acetamide, and, when boiled with water, yields diacetylurazole. *Acetylphenylurazole*, prepared by boiling phenylurazole with twice its weight of acetic anhydride, crystallises from benzene in leaflets, and melts at  $175^{\circ}$ . *Diacetylphenylurazole* is obtained by boiling the monacetyl derivative with 4 times its weight of acetic anhydride for 3 hours, and evaporating the solution in a vacuum over lime; it crystallises from benzene in white needles, and melts at  $164^{\circ}$ . When urazole is heated with acetic anhydride and sodium acetate for 3 hours, carbonic anhydride is liberated and *tetracetylhydrazide*,  $(\text{C}_2\text{H}_3\text{O})_4\text{N}_2$ , is formed; the latter, which may also be obtained by the action of acetic anhydride on hydrazine hydrate, melts at  $86^{\circ}$ , and crystallises from alcohol in long, rhombic crystals.

E. W. W.

**Derivatives of Monochloracetoxime.** By GEORG MATTHAIPOULOS (*Ber.*, 1898, **31**, 2396—2399. Compare Abstr., 1896, i, 520).—Chloracetoxime, when treated with alkalis, loses chlorine, but no definite compound is formed.

*Chloracetoximephenylcarbamide*, produced by adding phenylcarbimide to a solution of the oxime in benzene, crystallises from this solvent, melts at 112°, and decomposes and evolves gas at 150—160°.

*Triacetonylaminetrioxime*,  $N(CH_2 \cdot CMe \cdot NOH)_3$ , which is formed by the action of dry ammonia on an ethereal solution of chloracetoxime, melts at 184.5°, is soluble in hot water and alcohol, insoluble in ether, reduces silver nitrate, and dissolves in alkaline solutions, from which it is reprecipitated by carbonic anhydride.

The *methiodide* of the trioxime,  $N(CH_2 \cdot C \cdot Me \cdot NOH)_3 \cdot MeI$ , produced by warming the base with excess of methylic iodide, crystallises from alcohol, and melts and decomposes at 231°. The *ethiodide* is produced with greater difficulty and decomposes at 236°.

*Piperidylacetoxime*,  $C_5H_{10}N \cdot CH_2 \cdot CMe \cdot NOH$ , produced from the monochloroxime and piperidine in ethereal solution, crystallises from alcohol in lustrous, white crystals and melts at 123°; it reduces silver nitrate.

G. T. M.

**Condensation Products of Isobutaldehyde.** By ADOLF FRANKE and LEOPOLD KOHN (*Monatsh.*, 1898, **19**, 354—375).—The results previously obtained by the authors in conjunction with Brauchbar (Abstr., 1896, i, 404; 1897, i, 137; 1898, i, 353), are as follows. (1) Pure isobutaldehyde, obtained by the depolymerisation of paraisobutaldehyde by Fosseck's method, reacts with alcoholic potash (1 mol. to 3 mols. of the aldehyde), yielding isobutyric acid, a small quantity of the hydroxy-acid,  $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot COOH$ , and the octylglycol, 2:2:4-trimethylpentan-1:3-diol,  $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot OH$ . (2) The only product obtained by the action of a small quantity of alcoholic soda or potash at low temperatures ( $-20^\circ$ ) is isobutaldol. (3) The same product may be obtained by allowing the aldehyde to remain in contact with concentrated potassium carbonate solution for some time at the ordinary temperature. (4) Aqueous potassium hydroxide yields the aldol, glycol, and isobutyric acid. (5) When the aldehyde is heated with sodium acetate in sealed tubes, the products are Fosseck's compound,  $C_5H_{14}O$ , and the octylglycol isobutyrate,  $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot O \cdot CO \cdot CHMe_2$ . As these results do not agree with those obtained by different authorities, namely, Pfeiffer (*Ber.*, 1872, **5**, 699), Urech (Abstr., 1879, 520; 1880, 103, 538, 620), Fosseck (Abstr., 1882, 1279; 1884, 37), Perkin, jun. (Trans., 1883, **43**, 90), and Urbain (Abstr., 1896, i, 590), the authors have repeated the whole of the experiments described by these different authorities. They cannot corroborate Pfeiffer's statements, but confirm the results obtained by Brauchbar (Abstr., 1897, i, 137). They also dispute Urich's statement that a compound boiling at 154—157° can be obtained by the action of potassium carbonate on the aldehyde; they find that solid potassium carbonate in the cold yields the aldol, but, on boiling, the unaltered aldehyde is obtained, as at this temperature the aldol is re-converted into the aldehyde.

Fosseck's results, obtained by the action of sodium acetate solution on the aldehyde, are confirmed. The products are an oil boiling at  $150^{\circ}$ , the glycol isobutyrate (see above), and, under certain conditions, a third condensation product boiling at  $200^{\circ}$ . The formation of three neutral products as mentioned by Urbain by the action of warm alcoholic soda has not been confirmed. The chief product is a mixture of the octylglycol and its isobutyrate. On repeating Perkin's work, the authors find that results similar to Perkin's can only be obtained by using isobutaldehyde which has not been purified by conversion into its polymeric form. With an impure aldehyde not thus purified, a fraction boiling at  $153\text{--}157^{\circ}$  is obtained. This oil yields an *oxime*,  $\text{C}_7\text{H}_{12}\text{:N}\cdot\text{OH}$ , and thus indicates that the original oil is  $\text{C}_7\text{H}_{12}\text{O}$ ; it cannot be an aldehyde, since it is not oxidised on exposure to the air, its oxime gives no nitrile when treated with acetic anhydride, and it gives the iodoform reaction. All the facts indicate that the compound is a condensation product of isobutaldehyde and acetone, namely,  $\text{CHMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ . This constitution has been established by the actual synthesis of the compound from *pure* isobutaldehyde and acetone by using Perkin's condensation method; all the other fractions mentioned by Perkin were obtained in this condensation, and it is thus obvious that the aldehyde employed by Perkin must have contained acetone.

J. J. S.

**Synthesis of *r*-Glyceraldehyde.** By A. WOHL (*Ber.*, 1898, 31, 2394—2395. Compare *Abstr.*, 1898, i, 555).—*r*-Glyceraldehyde, obtained by the hydrolysis of the corresponding acetal with decinormal sulphuric acid, is a white, crystalline powder having a sweetish taste and melting at  $132^{\circ}$ ; it reduces silver nitrate in the cold. The molecular weight determination obtained by the freezing point method, in a freshly prepared solution, corresponds with 164, and only after two days does the number obtained, namely 90, agree with that of the simple molecule. This may be due to the fact that the compound in the solid state is bimolecular, and when dissolved only gradually changes, to the monomolecular condition.

G. T. M.

**Derivatives of Diacetyl.** By HARRY F. KELLER and PHILIPP MAAS (*Chem. Centr.*, 1898, i, 23—24; from *J. Franklin Inst.*, 1897, 144, 379—385).—By the action of cold hydrogen peroxide on dibromodiacetyl, a solution of bromacetic acid is formed which, on heating, decomposes into hydrogen bromide and glycollic acid. Amongst the mixture of acids obtained by the action of hot nitric acid on dibromodiacetyl, oxalic and bromacetic acids were detected. By the action of hydrogen peroxide on tetrabromodiacetyl, dibromacetic acid is not formed, but 30—40 per cent. of *pentabromacetone* is obtained, partly as a white, flocculent precipitate and partly in crystals which gradually separate from the solution. It crystallises from ether in long, colourless prisms which have a silky lustre, and from glacial acetic acid on addition of water in long, slender needles; it is insoluble in water, but very easily soluble in the ordinary organic solvents, has a peculiar penetrating odour, melts at  $72.8^{\circ}$ , and sublimes without apparent decomposition at a higher temperature. From the

mother liquor of the pentabromacetone, a small quantity of an oil, probably tribromacetone, was extracted with ether; it has a pungent odour and decomposes on heating. Tetrabromodiacetyl is not attacked even by fuming nitric acid.

Diacetylcyanhydrin, prepared by gently heating a mixture of diacetyl with a 30 per cent. solution of hydrogen cyanide, is a colourless oil which cannot be crystallised; attempts to convert it into the corresponding acid also failed. *Dibromodiacetyldicyanhydrin* crystallises from ether in lustrous crystals and melts and decomposes at  $177^{\circ}$ ; small quantities of the corresponding *acid amide* were obtained. *Tetrabromodiacetyldicyanhydrin* resembles the corresponding chlorine derivative. Attempts to prepare tetrachlorodiacetyl by the action of chlorine on diacetyl dissolved in carbon bisulphide or chloroform yielded only *dichlorodiacetyl*, which is very similar to dibromodiacetyl, crystallises in yellowish scales, melts at  $124.5^{\circ}$ , and is soluble in carbon bisulphide, chloroform, boiling light petroleum, and warm benzene.

E. W. W.

**Chloralacetones.** By L. GIGLI (*Gazzetta*, 1898, 28, ii, 83—86).—A mixture of acetylacetone and anhydrous chloral gradually solidifies to a mass of *acetylacetonechloral*,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{C}(\text{O})\text{Me}$ ; it crystallises in lustrous prisms melting at  $78-79^{\circ}$ .

*Benzoylacetonechloral*,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COPh}$ , is similarly obtained from benzoylacetone, and forms large, vitreous crystals melting at  $101-104^{\circ}$ .

*Benzoylacetoneoximechloral*,  $\text{CCl}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}(\text{NOH}) \cdot \text{CH} : \text{CHPh}$ , prepared by the direct combination of chloral with benzoylacetoneoxime, forms lustrous crystals melting at  $113-114^{\circ}$ . W. J. P.

**Electrolysis of the Sodium Salts of Halogen-substituted Fatty Acids.** By JULIUS TROEGER and E. EWERS (*J. pr. Chem.*, 1898, [ii], 58, 121—128).—The electrodes consisted of spirally rolled platinum foil, the cathode being placed in a small, porous cell, and the whole apparatus kept cool with ice; the E. M. F. employed was 16 volts, the current about 0.5 ampère. In the case of sodium  $\alpha$ -dichloropropionate, an oily product was obtained at the anode; it solidified, but did not melt when heated, subliming instead; it is an unstable substance, and appears to be  $\alpha$ -dichlorethylic  $\alpha$ -dichloropropionate,  $\text{CMeCl}_2 \cdot \text{COO} \cdot \text{CMeCl}_2$  (compare Elbs and Kratz, *Abstr.*, 1897, i, 553). With sodium dichloroacetate, a similar product seems to be formed, but it is even more unstable, hydrochloric acid and carbonic oxide being formed at the anode. With sodium chloroacetate, no oily product was obtained. With sodium  $\beta$ -iodopropionate, iodoform was obtained at the anode.

C. F. B.

**Manufacture and Applications of Lactic Acid.** By ALAN A. CLAFLIN (*J. Soc. Chem. Ind.*, 1897, 16, 516—518).—In order to determine its complete decomposition by the lactic acid bacillus, the solution of dextrose should have a sp. gr. ranging between 1.05 and 1.075; it seems advantageous if 10—15 per cent. of the saccharine matter consists of cane-sugar. The amount of nitrogen needed for the

growth of the ferment is about 2 per cent. of the weight of sugar employed, and is best added in the form of the extract obtained by treating bran with boiling water and dilute acid. The fermentation, which should take place at  $45^{\circ}$ , is best started by means of a pure culture of the lactic acid bacillus obtained during a previous fermentation; to prevent butyric fermentation, the acidity must be rigidly confined between 0.02 and 0.5 per cent. by adding chalk or milk of lime. In from 3—6 days, the fermentation is completed, over 98 per cent. of the sugar being converted into lactic acid; the ferment is then destroyed by heating to  $100^{\circ}$ , the solution evaporated, and the calcium lactate purified by recrystallisation. The free acid is obtained in a pure state by decomposing the aqueous calcium lactate with sulphuric acid, removing any excess of the latter by means of baryta, and evaporating the solution until it contains about 50 per cent. of lactic acid; little of the latter is lost during evaporation, although about 7 per cent. is converted into lactic anhydride. W. A. D.

**Lichenostearic Acid.** By HUGO SINNHOLD (*Arch. Pharm.*, 1898, 236, 504—522).—As the observations of previous workers on lichenostearic acid (from Iceland moss, "*Cetraria Islandica*") are not in accord, the author has submitted the acid to a further investigation (compare Hesse, *Abstr.*, 1898, i, 534). For the preparation of the acid, the moss was extracted with ether, and, after evaporation of the solvent, the dark green residue was purified by treatment first with alcohol and then with light petroleum, in which the acid is insoluble.

*Lichenostearic acid*,  $C_{18}H_{31} \cdot COOH$ , crystallises from dilute alcohol in nacreous tetragonal or rhombic plates, melts at  $124.5$ — $125^{\circ}$ , and resolidifies at  $120$ — $122^{\circ}$ ; it does not contain nitrogen, is almost tasteless, and is not acted on by bromine or potassium permanganate. The *potassium* and *ammonium* salts are crystalline, and the *silver*, *copper*, *calcium*, and *barium* salts are amorphous. The *methylic* salt separates from alcohol in colourless, flat prisms melting at  $96$ — $97^{\circ}$ , and the *ethylic* salt crystallises with difficulty and melts at  $60^{\circ}$ .

*Lichenosterylic acid*,  $C_{17}H_{33}O \cdot COOH$ , obtained from the above acid by boiling for some hours with a 10 per cent. solution of potassium hydroxide, crystallises from alcohol in broad, rhombic leaflets melting at  $83.5$ — $84^{\circ}$ , and in its behaviour towards reagents resembles the parent substance. The *silver* and *copper* salts are described. The acid is not acted on by sodium amalgam, and when heated with amorphous phosphorus and hydriodic acid in sealed tubes at  $220$ — $250^{\circ}$ , is converted into an oil containing phosphorus.

The constitution of these acids remains doubtful, the want of material rendering further experiments impossible. A. W. C.

**Preparation of Glyceric Acid.** By ZINNO (*Chem. Centr.*, 1898, i, 26; from *Pharm. Centr.-H.*, 38, 780).—The author prepares glyceric acid by adding nitric acid drop by drop to a hot mixture of 200 grams of glycerol, 200 grams of water, and 100 grams of red lead, which is kept stirred and not heated to above  $100^{\circ}$ . When the whole of the red lead is decolorised, the liquid is filtered through a hot filter, the residue washed with hot water, the filtrate concentrated in the steam bath, and then stirred with a slight excess

of sulphuric acid of sp. gr. = 1.53. The filtrate from the lead sulphate, after treatment with barium hydroxide and filtering, is finally concentrated in a vacuum over sulphuric acid, and any precipitated barium nitrate filtered off.

E. W. W.

**Preparation of Amides.** By OSSIAN ASCHAN (*Ber.*, 1898, 31, 2344—2350).—Amides of organic acids have been hitherto obtained either by distillation of the corresponding ammonium salts, by decomposition of the alkylic salts with ammonia, or by the action of ammonia or ammonium carbonate on the acid chlorides. Hofmann made use of a modification of the first method, which consisted in heating the ammonium salts under pressure at 230°.

The mixture of acid chloride and phosphorus oxychloride obtained on treating the organic acid with phosphorus pentachloride, when added to well cooled ammonia, yields the amide, but although this method renders the isolation of the chloride unnecessary, it has its disadvantages. The phosphorus oxychloride always produces a certain amount of nitrile, and, moreover, the additional quantity of ammonia necessary to decompose the phosphorus compound is three times that required to form the amide.

Instead of phosphorus pentachloride, the author treats the acid with a slight excess of the trichloride, and the action is accelerated by warming; the mixture is then cooled in ice, and the organic chloride, decanted from the viscid phosphorous acid, is slowly added to a cooled solution of ammonia (25—28 per cent.). The amide thus produced is isolated by suitable means, depending on the nature of the compound. The amides of acetic, propionic, butyric, isobutyric, isovaleric, isocaproic, oenanthylic, caprylic, stearic, oleic and sebacic acids are readily obtained by this method, and the following are described for the first time.

*Undecylenamide* crystallises from dilute alcohol, and melts at 84.5—85.5°; it possesses a characteristic odour.

*Suberamide*, obtained by heating suberic acid with phosphorus trichloride, and decomposing the chloride in the usual way, crystallises from water in ill-defined prisms, sinters at 215°, and melts at 216—217°.

G. T. M.

**Urethanes.** By JOHANNES THIELE and FRANKLAND DENT (*Annalen*, 1898, 302, 245—272. Compare Thiele and Lachmann, *Abstr.*, 1896, i, 207).—*Methylic nitrocarbamate*,  $\text{NO}_2 \cdot \text{NH} \cdot \text{COOMe}$ , prepared by treating a solution of methylic carbamate in sulphuric acid with ethylic nitrate at  $-5^\circ$ , forms colourless, lustrous plates or monoclinic prisms, and melts at  $88^\circ$ ; it decomposes at  $120$ — $130^\circ$ , and yields methylic phenylcarbamate or diphenylcarbamide with warm aniline. The *ammonium* derivative crystallises from warm water in colourless needles, and the *potassium* derivative forms large prisms; the *mercury* and *silver* derivatives crystallise in small needles.

*Methylic nitrosocarbamate*,  $\text{NO} \cdot \text{NH} \cdot \text{COOMe}$ , obtained by reducing methylic nitrocarbamate with zinc dust and glacial acetic acid, crystallises in yellow needles from a concentrated solution in ether to which petroleum has been added; it melts and decomposes at  $61^\circ$ . The



*ammonium* derivative melts and decomposes at  $105^{\circ}$ ; the *silver* derivative decomposes quickly in light. Water, dilute sulphuric acid, and aqueous mellitic acid eliminate nitrogen from the ethereal salt, the gas being accompanied by carbonic anhydride in the case of the agent last named; sulphuric acid also gives rise to methyl hydrogen sulphate, but no trace of ethyl hydrogen sulphate is obtainable from ethylic nitrosocarbamate under the same conditions. The authors regard it as possible that methylene is the initial product in the decomposition of methylic nitrosocarbamate, and in order to give support to this view, they have studied the behaviour of nitrosourethane towards dilute sulphuric acid in presence of bromine, and also the action of water and dilute acids on ethylic chlorocarbonate; in the first case, ethylenic bromide, and in the second case, ethylene, are formed, and no trace of ethylenic derivatives.

*Benzylic chlorocarbonate*,  $\text{Cl}\cdot\text{COO}\cdot\text{CH}_2\text{Ph}$ , obtained on adding benzylic alcohol drop by drop to its own weight of carbonylic chloride at  $-8^{\circ}$ , is a colourless oil with penetrating odour; it boils, and in part decomposes at  $103^{\circ}$ , under a pressure of 19–20 mm., and at  $155^{\circ}$  is completely resolved into carbonic anhydride and benzylic chloride. Ammonia converts it into benzylic carbamate.

*Paranitrobenzylic chlorocarbonate*,  $\text{Cl}\cdot\text{COO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , prepared by the action of carbonylic chloride on paranitrobenzylic alcohol, crystallises from light petroleum in colourless needles, and melts at  $32^{\circ}$ ; the substance is resolved into carbonic anhydride and paranitrobenzylic chloride when heated. *Paranitrobenzylic carbamate*,  
 $\text{NH}_2\cdot\text{COO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ,

obtained by treating the foregoing compound with ammonia, crystallises from benzene in pale yellow leaflets melting at  $154^{\circ}$ . *Paranitrobenzylic nitrocarbamate*,  $\text{NO}_2\cdot\text{NH}\cdot\text{COO}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , formed by the action of ethylic nitrate on paranitrobenzylic carbamate dissolved in sulphuric acid, crystallises from benzene in pale yellow needles and melts at  $140^{\circ}$ . The *ammonium* derivative crystallises in yellow plates and needles which melt and decompose at  $153^{\circ}$ ; the *potassium* derivative forms prisms, the *mercury* derivative is amorphous, and the *silver* derivative crystallises in needles which resist the action of light. The *aniline* derivative separates from benzene in lustrous, monosymmetric plates, and melts and decomposes at  $147^{\circ}$ ; the action of heat resolves it into nitrous oxide and *paranitrobenzylic phenylcarbamate*,  $\text{NHPh}\cdot\text{COO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , which crystallises from alcohol in long, colourless needles and melts at  $123^{\circ}$ .

The *chlorocarbonate* of ethylic glycollate,  $\text{Cl}\cdot\text{COO}\cdot\text{CH}_2\cdot\text{COOEt}$ , obtained by the action of carbonylic chloride on ethylic glycollate at  $60^{\circ}$  in sealed tubes, is a liquid of penetrating odour, which boils at  $113^{\circ}$  and  $182$ – $183^{\circ}$  under pressures of 80 mm. and 714 mm. respectively, undergoing slight decomposition at the higher temperature. The *carbamate* of ethylic glycollate,  $\text{NH}_2\cdot\text{COO}\cdot\text{CH}_2\cdot\text{COOEt}$ , produced by treatment with ammonia, crystallises from benzene in large prisms and melts at  $61^{\circ}$ . The *nitrocarbamate*,  $\text{NO}_2\cdot\text{NH}\cdot\text{COO}\cdot\text{CH}_2\cdot\text{COOEt}$ , prepared by the action of ethylic nitrate on the carbamate dissolved in sulphuric acid, crystallises from benzene in slender, colourless leaflets and melts at  $80^{\circ}$ ; the *silver* derivative crystallises from hot

water in transparent leaflets, and the *potassium* derivative forms small needles.

The *chlorocarbonate* of ethylic lactate,  $\text{Cl}\cdot\text{COO}\cdot\text{CHMe}\cdot\text{COOEt}$ , is a liquid of penetrating odour which boils at  $91^\circ$  and at  $180^\circ$ , under pressures of 19 mm. and 714 mm. respectively; ammonia converts it into the *carbamate*,  $\text{NH}_2\cdot\text{COO}\cdot\text{CHMe}\cdot\text{COOEt}$ , which crystallises from benzene in attenuated leaflets, and melts at  $65.5^\circ$ . The *nitrocarbamate*,  $\text{NO}_2\cdot\text{NH}\cdot\text{COO}\cdot\text{CHMe}\cdot\text{COOEt}$ , separates from benzene in small, monosymmetric plates, and melts at  $68^\circ$ ; the *silver* derivative forms large prisms and decomposes at  $50^\circ$ .

The urethanes of fatty alcohols, excepting methylic carbamate, yield olefines under the influence of nitrous acid, which decomposes them on the principle of the following equation,  $2\text{NH}_2\cdot\text{COOEt} + 2\text{HNO}_2 = 2\text{CO}_2 + 2\text{N}_2 + \text{C}_2\text{H}_5\cdot\text{OH} + \text{C}_2\text{H}_4 + 3\text{H}_2\text{O}$ . This reaction has been studied in the case of the urethanes derived from ethylic, propylic, isopropylic, and isobutylic alcohols. Benzylic and paranitrobenzylic carbamates yield the respective alcohols along with nitrogen and carbonic anhydride; allylic carbamate and the carbamates of ethylic glycolate and ethylic lactate also fail to yield unsaturated hydrocarbons. M. O. F.

**$\psi$ -Carbamides.** By ERNST SCHMIDT (*Arch. Pharm.*, 1898, 236, 441—445. Compare next abstract).—The researches of Falke (*Diss. Marburg*, 1893), Gadamer (*Abstr.*, 1896, i, 140, 414), and Schacht (*Abstr.*, 1898, i, 12) have shown that thiocarbamide, thiosinamine (allylthiocarbamide), ethylenethiocarbamide, and trimethylenethiocarbamide can exist in two tautomeric forms; the last two substances cannot, however, be directly converted into  $\psi$ -carbamides, as is the case with thiosinamine and other alkylated thiocarbamides.

The conversion of allylthiocarbamide into the  $\psi$ -form can be brought about, as Gabriel (*Abstr.*, 1890, 127) has shown, by fuming hydrobromic or hydrochloric acids at  $100^\circ$ , or (compare Gadamer) by the action of bromine or iodine at ordinary temperatures.

The bromopropylencarbamide of Andreasch is shown by Rundqvist (compare next abstract) to be a bromine substitution product of Gabriel's  $\psi$ -allylcarbamide; especially is this shown by its synthesis from dibromopropylamine and potassium cyanate.

Diallylcarbamide (sinapoline) and diallylthiocarbamide are acted on by bromine and iodine with formation of ring compounds, namely, halogen substitution products of  $\psi$ -carbamides or  $\psi$ -thiocarbamides.

A. W. C.

**Allyl Substituted Carbamides and Thiocarbamides.** By CARL RUNDQVIST (*Arch. Pharm.*, 1898, 236, 445—447. Compare preceding abstract).—Thiosinamine dicyanide, first obtained by Maly (*J. pr. Chem.*, 1868, 413), is best prepared by passing cyanogen into an aqueous solution of thiosinamine; it crystallises from ethylic acetate in glistening, bronze-coloured, microscopic plates, and its alcoholic solution does not show any green fluorescence, as Maly has stated to be the case. It decomposes, without previously melting, when heated in a capillary tube to  $193^\circ$ , and gives precipitates with the salts of the heavy metals, but is not acted on by picric or phosphomolybdic acids.

When warmed with dilute sulphuric or hydrochloric acids, it is converted into allylthioparabanic acid; this crystallises in long, lemon-yellow needles, melts at  $89^{\circ}$ , and gives precipitates with platinic, mercuric, auric, and cupric chlorides, which are apparently not homogeneous but mixtures of several substances. With silver nitrate, a precipitate is formed which, on gently warming, is decomposed, sulphur being eliminated and silver allylparabanate formed.

*Allylparabanic acid*, obtained from the silver salt by the action of hydrogen sulphide, separates in transparent, glistening, needle-shaped crystals melting at  $140^{\circ}$  and is identical with the acid prepared by the action of allylic iodide on silver parabanate.

Allylthioparabanic acid is converted into potassium oxalate and thiosinamine by the action of potassium hydroxide, and in presence of sodium carbonate, to neutralise the nitric acid formed, silver nitrate converts it into allylcarbamide, melting at  $85^{\circ}$ , and oxalic acid. Maly (*loc. cit.*) gives the melting point of this substance as  $141^{\circ}$ , and the author concludes that Maly's compound must have been either silver oxalate (m. p.  $140^{\circ}$ ) or a mixture of the decomposition products of allylcarbamide.

The allylcarbamide from which the following compounds were prepared was obtained by Andreasch's method, namely, the action of potassium isocyanate on allylamine sulphate. It is an oil which, on cooling, solidifies to a mass of radiating needles, melts at  $85^{\circ}$ , and resembles carbamide in its behaviour towards acids, but differs from it in not so readily forming salts and double salts.

Dibromopropylcarbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{Br}$ , formed by the direct action of bromine on allylcarbamide, is a white, crystalline powder melting at  $109^{\circ}$ , and agrees in its properties with those ascribed to it by Andreasch (*Monatsh.*, 5, 39), as do also bromo- $\psi$ -allylcarbamide and its hydrobromide. The former gives an *aurichloride*,  $\text{C}_4\text{H}_7\text{BrN}_2\text{O} \cdot \text{HAuCl}_4$ , separating in glistening, dark orange-red crystals melting at  $120.5^{\circ}$ , and a *picrate* crystallising in yellow needles and melting at  $175^{\circ}$ .

*Iodo- $\psi$ -allylcarbamide hydriodide*,  $\text{C}_4\text{H}_8\text{N}_2\text{OI}_2$ , obtained by the action of a solution of iodine in potassium iodide on allylcarbamide, separates in well formed, transparent crystals melting and decomposing at  $105$ – $108^{\circ}$ . Silver chloride converts it into the corresponding *hydrochloride*, forming thin, exceedingly soluble needles, melting at  $111^{\circ}$ . The *platinochloride* forms beautiful yellow crystals; the *aurichloride*, yellowish-red crystals melting at  $140^{\circ}$ , and the *picrate* transparent, yellowish-green needles melting at  $159^{\circ}$ . The *free base* obtained from the hydriodide by the action of potassium hydroxide, crystallises in glistening plates, and melts at  $104$ – $106^{\circ}$  with separation of iodine.

*Hydroxy- $\psi$ -allylcarbamide* was prepared from the iodine base by the action of silver nitrate, and identified as its *platinochloride* and *aurochloride*. The former,  $(\text{OH} \cdot \text{C}_4\text{H}_7\text{N}_2\text{O})_2 \cdot \text{H}_2\text{PtCl}_6$ , crystallises in dark coloured, tetragonal leaflets, and the latter is a red-brown, oily liquid, solidifying to a mass of yellowish needles.

*Bromo- $\psi$ -allylcarbamide methiodide* crystallises from methylic alcohol in glistening crystals, and by digestion with silver chloride is converted into the corresponding chloride, giving a *platinochloride*

which separates in orange crystals. *Iodo-ψ-allylthiocarbamide methiodide* separates from methylic alcohol in transparent, yellow crystals melting at 119°, and gives a *platinochloride* forming yellowish-red, glistening crystals.

Cyanogen has no action on allylcarbamide. When reduced with sodium amalgam or zinc and acetic acid, bromo-ψ-allylcarbamide, hydrobromide, or the corresponding iodine compound, is converted into allylcarbamide, so that these substances must have a constitution similar to that of thiosinamine bromide; this view is further supported by the synthesis of bromo-ψ-allylcarbamide from dibromopropylamine and potassium isocyanate.

Sinapoline (diallylcarbamide) is best prepared by Will's method (*Annalen*, 1844, 52, 26). With platinic, auric, and mercuric chlorides, it gives amorphous precipitates, but nothing with picric or tannic acid. It is readily acted on by bromine, and from the product, after treatment with silver chloride, an *aurichloride* is obtained as a viscid mass, and a *picrate* as a fine, crystalline powder melting at 121°, which is a proof of the fact that, by the action of bromine, sinapoline undergoes a rearrangement, with formation of a ring compound. Iodine also combines with sinapoline at the ordinary temperature. Diallylthiocarbamide, prepared according to Hecht's directions (*Abstr.*, 1890, 477), forms large, glistening leaflets melting at 49.5°, and behaves towards acids and the salts of heavy metals just as diallylcarbamide does. With bromine, it forms a dark coloured, syrupy bromide, which gives a precipitate with silver nitrate, proving that ring formation has taken place. After decomposition with silver chloride, it gives an aurochloride and platinochloride as amorphous precipitates which were not analysed. In its behaviour towards iodine, it fully resembles sinapoline, and does not yield a compound with cyanogen.

A. W. C.

**Sulphonation of the Paraffins.** By R. A. WORSTALL (*Amer. Chem. J.*, 1898, 20, 664—675).—The results described below show that aliphatic as well as benzenoid hydrocarbons are capable of direct sulphonation; although cold fuming sulphuric acid is without action on hexane, heptane, and octane, it rapidly effects sulphonation when added to the hydrocarbons at their boiling points, monosulphonic acids being produced. Disulphonic acids are sometimes formed in small quantity under these conditions, but are prepared by passing sulphuric anhydride through the boiling paraffins.

Normal hexanesulphonic acid, prepared by adding successive small portions of fuming sulphuric acid to the boiling hydrocarbon, is a thick, light-brown liquid, which is very soluble in water and alcohol, but insoluble in ether; from 30—40 per cent. only of the theoretical quantity is obtained, the remainder of the hydrocarbon being completely oxidised. The barium salt,  $(C_6H_{13}SO_3)_2Ba$ , separates in brownish plates, and is extremely soluble in water, but insoluble in alcohol and ether, and the *lead* salt closely resembles it. *Normal hexanedisulphonic acid*,  $C_6H_{12}(SO_3H)_2$ , is a thick syrup, extremely soluble in water and very deliquescent; it is insoluble in light petroleum and ether, but soluble in hot benzene and alcohol. The

barium salt,  $C_6H_{12}(SO_3)_2Ba$ , is golden-yellow, very soluble in water, and very deliquescent; the lead salt,  $C_6H_{12}(SO_3)_2Pb$ , has similar properties.

From normal heptane, the same yield of monosulphonic acid is obtained as from normal hexane; the barium salt,  $(C_7H_{15}SO_3)_2Ba$ , the lead salt,  $(C_7H_{15}SO_3)_2Pb$ , and the free acid closely resemble the corresponding derivative of hexane, as also do *normal heptanedisulphonic acid*,  $C_7H_{14}(SO_3H)_2$ , its barium salt,  $C_7H_{14}(SO_3)_2Ba$ , and its lead salt,  $C_7H_{14}(SO_3)_2Pb$ , the derivatives which correspond with them.

*Normal octanesulphonic acid*,  $C_8H_{17}SO_3H$ , its barium salt,  $(C_8H_{17}SO_3)_2Ba$ , its lead salt,  $(C_8H_{17}SO_3)_2Pb$ , and *normal octanedisulphonic acid* closely resemble the corresponding derivatives of hexane and heptane.

On passing sulphuric anhydride into boiling hexane and heptane, there is formed, in each case, in addition to the disulphonic acid, a very small quantity of a brown, brittle *solid*, which is insoluble in water and all organic solvents; from normal octane, a considerable quantity of a similar substance is obtained. The analyses show that these compounds belong to a regular series, and their richness in oxygen suggests that they are possibly oxysulphones.

W. A. D.

**Aliphatic Sulphonic Acids. II.** By ELMER P. KOHLER (*Amer. Chem. J.*, 1898, 20, 680—695. Compare *Abstr.*, 1898, i, 68).—*Ethylenesulphonic acid*,  $CH_2:CH \cdot SO_3H$ , is prepared by boiling  $\alpha\beta$ -ethanedisulphonic chloride with five times its weight of water until completely dissolved; the solution is evaporated until the whole of the hydrochloric acid formed has been removed, then neutralised with solid ammonium carbonate, and evaporated to dryness. After adding a small quantity of absolute alcohol and again evaporating to dryness, the residue is boiled with absolute alcohol and filtered; ammonium ethylenesulphonate dissolves in the alcohol, and is thus freed from ammonium ethanedisulphonate, which is insoluble. Ethylenesulphonic acid, obtained from its ammonium salt by boiling the latter with lead carbonate, decomposing the lead salt thus obtained with hydrogen sulphide, and evaporating on the water-bath, and over sulphuric acid, is an oily liquid which is very soluble in water, alcohol, and glacial acetic acid, but only sparingly in ether and chloroform. It is formed when  $\alpha\beta$ -bromethanesulphonic chloride is distilled under increased pressure, hydrogen bromide being evolved, and can be prepared by heating the acetyl derivative of potassium, sodium, or barium isethionate at  $185^\circ$ , acetic acid being also formed. *Ammonium ethylenesulphonate*,  $CH_2:CH \cdot SO_3 \cdot NH_4$ , crystallises from dilute alcohol in large, orthorhombic plates, and from boiling absolute alcohol in short prisms; when heated, it melts completely at  $156^\circ$ , but immediately resolidifies; the *product* is colourless, reacts with bromine and potassium permanganate in the cold, evolves ammonia when heated with alkalis, and is decomposed when heated a few degrees above  $156^\circ$ . *Potassium ethylenesulphonate*,  $C_2H_3SO_3K$ , is very soluble in water, and crystallises from the latter in large plates, and from alcohol in slender needles; the *sodium salt*,  $C_2H_3SO_3Na$ , closely resembles it, whilst the *barium*

salt,  $(C_2H_3SO_3)_2Ba + H_2O$ , is insoluble in alcohol and crystallises from water in minute needles. The *lead* salt,  $(C_2H_3SO_3)_2Pb + 2H_2O$ , is only sparingly soluble in cold water, crystallises in hard, lustrous prisms, and, when heated, is decomposed after losing its water of crystallisation.

*Ethylenesulphonic chloride*,  $CH_2:CH \cdot SO_2Cl$ , prepared by the action of phosphorus pentachloride on the potassium salt suspended in chloroform, is an oily liquid which boils at  $118-120^\circ$ , with slight decomposition under a pressure of 250 mm., and is easily hydrolysed by boiling water.

Ethylenesulphonic acid is completely oxidised by a cold acid solution of potassium permanganate; in presence of alkali, the action is the same, but takes place more slowly, and the same is the case with all other oxidising agents.

Ethylenesulphonic acid is reduced only with difficulty; it is converted by sodium amalgam into isethionic acid, by the addition of the elements of water, but remains unacted on when boiled with zinc and dilute sulphuric acid during 24 hours. When, however, it is heated with hydriodic acid and phosphorus for 10 hours at  $170^\circ$ , it is converted into ethanesulphonic acid, isethionic acid being also formed.

Although ethylenesulphonic acid is not changed by boiling during 10 hours with water, it is converted into isethionic acid when boiled with dilute alkalis, or heated with water at  $150^\circ$  during several hours. The acid formed was identified by its sulphonic chloride, and yielded a potassium salt which melted at  $190^\circ$ , whereas Liebig has stated that potassium isethionate melts at  $350^\circ$ ; on repeating the latter's experiments, however, a salt was obtained which melted at  $190^\circ$ .

Potassium  $\alpha\beta$ -chloroethanesulphonate is formed together with some isethionate, by heating potassium ethylenesulphonate during 5 hours at  $130^\circ$  with concentrated hydrochloric acid; hydrobromic acid, under the same conditions, gives rise to *potassium  $\alpha\beta$ -bromethanesulphonate*. The latter crystallises from water in orthorhombic plates, and from absolute alcohol in thin, friable laminae; it is converted by silver oxide into potassium isethionate. The corresponding *sodium  $\alpha\beta$ -bromethanesulphonate* is prepared by adding sodium sulphite to ethylenic bromide dissolved in very dilute alcohol. Details concerning this will be published later.

Bromine acts by substitution on aqueous potassium ethylenesulphonate, *potassium bromethylenesulphonate*,  $C_2H_2Br \cdot SO_3K$ , being formed; this crystallises from boiling absolute alcohol in long, colourless needles, is extremely hygroscopic, and is very soluble in water. It is decomposed by dilute barium hydroxide, barium sulphite and bromide being formed; from the solution obtained, ether extracts a gum-like *substance*, which hardens in the air to a horn-like mass of varying composition. It is not changed by silver oxide, or by a cold solution of potassium permanganate, but is oxidised, when heated with the latter, to carbonic anhydride and water, whilst nitric acid gives rise, in addition, to a small quantity of oxalic acid. It appears probable, from the manner of its decomposition by barium hydroxide, that the potassium bromethylenesulphonate described above has the structure  $CH_2:CBBr \cdot SO_3K$ .

W. A. D.

**Acetylene Derivatives.** By HUGO ERDMAN and PAUL KÖTHNER (*Zeit. anorg. Chem.*, 1898, 18, 48—58).—When acetylene is passed over finely divided copper heated to 400—500°, it is decomposed into hydrogen and carbon, the latter being deposited in the graphitic condition. At lower temperatures (below 250°), the copper combines with the gas to form a yellowish-brown *compound*, which, unlike Söderbaum's cupric acetylide (Abstr., 1897, i, 309), is not explosive. The new substance is more conveniently prepared by heating finely divided cuprous oxide in a current of acetylene at 250°; it is exceedingly voluminous, and its composition corresponds with the formula  $C_{44}H_{64}Cu_3$ ; when heated with excess of zinc dust, it yields 20 per cent. of an oil boiling between 190—250°, and possessing an odour like Caucasian naphtha; if the mixture is heated to a higher temperature, aromatic hydrocarbons appear in the distillate and naphthalene is obtained, whilst a portion which dissolves in caustic soda has properties resembling those of cresol.

It is difficult to obtain well defined acetylides of the metals of the potassium group. Rubidium, although acted on by acetylene at low temperatures, gives rise to no definite product. Zinc and mercury are scarcely acted on, and iron, like copper, acts catalytically, inducing condensation to oily hydrocarbons.

Solutions of thallium, lead, cadmium, iron, nickel, cobalt, platinum, iridium, and rhodium salts give no precipitate with acetylene; gold chloride gives a black precipitate, which, on warming, changes to metallic gold, palladium chloride gives a brown precipitate which is soluble in ammonia, in each case the precipitation being accompanied by the production of an aldehydic odour.

Copper acetate and silver nitrate yield brownish-red and white precipitates respectively.

*Mercuric carbide nitrate*,  $HgC:CHg, HgNO_3 + H_2O$ , produced by saturating a hot solution of mercuric nitrate with acetylene, separates in small, white crystals, and differs from Keiser's silver analogue,  $C_2Ag_2, AgNO_3$ , in containing  $H_2O$ . It resembles Poleck and Thümmel's mercury derivative of vinyl alcohol (Abstr., 1890, 118), and yields acetaldehyde on treatment with dilute acids.

Acetaldehyde is produced when acetylene is passed through a suspension of mercuric oxide in boiling phosphoric acid of sp. gr. = 1.15, or in 30 per cent. sulphuric acid. G. T. M.

**Action of Acetylene on Mercuric Nitrate.** By PAUL KÖTHNER (*Ber.*, 1898, 31, 2475).—Hofmann has recently (Abstr., 1898, i, 635) described a crystalline substance obtained by the action of acetylene on a solution of mercuric nitrate. The author had previously studied this compound, obtaining results similar to those of Hofmann, and had drawn attention to the relationship of the substance to vinylic alcohol and acetaldehyde (see Köthner, *Halle. a. S. Frühjahr*, 1896; and Erdmann and Köthner, preceding abstract).

The differences in the composition assigned to the substance by Hofmann and by the author may be due to a slight difference in the conditions of preparation, and the author states his intention of re-examining the question from this point of view. A. L.

**A Compound of Acetylene with Cuprous Oxychloride.** By R. CHAVASTELON (*Compt. rend.*, 1898, 127, 68—69. Compare Abstr., 1898, i, 613).—The crystalline compound of acetylene with cuprous chloride,  $C_2H_2, Cu_2Cl_2$ , is decomposed by water, with production of a violet compound; acetylene is, at the same time, slowly liberated, and the liquid is found to contain free hydrochloric acid, which limits the decomposition. The violet substance is best prepared by digesting the compound  $C_2H_2, Cu_2Cl_2$  with a large excess of water, saturated with carbonic anhydride, out of contact with air. The crystals are washed with absolute alcohol and anhydrous ether, and finally dried over calcium chloride in an atmosphere of carbonic anhydride. Estimation of the copper and chlorine, and the measurement of the volume of acetylene which the compound yields when treated with concentrated hydrochloric acid, show that it has the composition  $C_2H_2, Cu_2Cl_2, Cu_2O$ .  
N. L.

**Combination of Carbon Compounds with Mercuric Sulphate.** By GEORGES DENIGÈS (*Compt. rend.*, 1898, 126, 1868—1871).—The carbon compounds capable of combining with mercuric sulphate in acid solution (Abstr., 1898, i, 546) are thiophen and its derivatives, the olefines, terpenes, and hydrocarbons of the benzene series and their respective derivatives, aldehydes, and ketones; they are all characterised by the existence of latent valencies or the occurrence of double bonds.

Acetone yields the calculated quantity of a white, crystalline compound,  $C_3H_6O, 3HgO, 2HgSO_4$ , completely soluble in hydrochloric acid, and its homologues of low molecular weight yield similar compounds, but in the case of ketones of high molecular weights the reaction is complex, condensations taking place and secondary products being formed. When the compounds are suspended in water and treated with hydrogen sulphide, the ketone is liberated.

Acetylacetone, pyruvic acid, acetonedicarboxylic acid, &c., yield similar compounds, which will be described subsequently.

C. H. B.

**Derivatives of the Naphthene or Cyclohexane Series.** By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1898, 302, 1—42. Compare Abstr., 1898, i, 637; also von Baeyer, Abstr., 1894, i, 174).—The author supplies an historical account of the information to be found on the subject of hexanaphthene. By reducing the iodide which boils at  $193^\circ$ , with a copper-zinc couple in hydrochloric acid, the hydrocarbon is obtained having the sp. gr. = 0.7902 at  $0^\circ/0^\circ$ , or 0.7727 at  $20^\circ/0^\circ$ ; it boils at  $80.5\text{—}81^\circ$  under a pressure of 761.5 mm. Hexanaphthene has an odour of pure "benzine," which is less penetrating than that of petroleum; it undergoes little change in contact with a mixture of nitric and sulphuric acids at the ordinary temperature, but at  $100^\circ$  very vigorous action takes place. The hydrocarbon is quite indifferent towards cold fuming nitric acid, and even the boiling liquid acts slowly, producing chiefly adipic acid.

*Chlorohexanaphthene*,  $C_6H_{11}Cl$ , is prepared by the action of moist chlorine on the hydrocarbon in diffused light; if the operation is con-



ducted with the dry gas, it is necessary to heat the liquid until it nearly boils, but the method is less satisfactory owing to the production of more heavily chlorinated derivatives. It is a colourless liquid, and is quite stable in the dry state, but becomes yellow and then brown when contaminated with water or with hydrogen chloride. The substance boils at  $142^{\circ}$  and  $143^{\circ}$  under pressures of 750 mm. and 768 mm. respectively; it has a sp. gr. = 0.990 at  $0^{\circ}/0^{\circ}$  or 0.973 at  $20^{\circ}/0^{\circ}$ . Boiling alcoholic potash converts it with difficulty into naphthylene and the ether  $C_6H_{11}\cdot OEt$ .

*Chloronaphthylene* [*chlorocyclohexene*],  $C_6H_9Cl$ , obtained by the action of phosphorus pentachloride on ketoexamethylene, boils at  $142$ — $143^{\circ}$ , and has an agreeable odour; it decolorises the vapour of bromine.

On fractionating the less volatile products of the action of chlorine on hexanaphthene, isomeric *dichloro*-derivatives are obtained. Two portions of the distillate boiling at  $192$ — $194^{\circ}$  and  $196$ — $198^{\circ}$  have the sp. gr. = 1.167 and 1.172 respectively at  $15^{\circ}/15^{\circ}$ ; the results of analysis agree with the requirements of the formula  $C_6H_{10}Cl_2$ .

Iodoexamaphthene boils at  $193^{\circ}$  under a pressure of 765 mm., decomposing slightly at that temperature; it is a pale yellow liquid, and quickly becomes coloured with iodine when exposed to light.

Bromine acts on hexanaphthene at  $110^{\circ}$  without producing a monobromo-derivative. When the halogen is employed in molecular proportion, upwards of half the hydrocarbon remains unchanged, the remainder being converted into polybromo-derivatives. In presence of aluminium bromide, a product derived from methylpentamethylene is obtained, and appears to be a mixture of the compounds  $C_6H_4Br_8$  and  $C_6H_3Br_7$ ; it melts at  $120$ — $121^{\circ}$ , and is identical with the substance obtained by Kistner from methylpentamethylene (hexahydrobenzene), bromine, and aluminium bromide. This affords a new instance of conversion of the hexamethylene into the pentamethylene ring.

*Nitrohexanaphthene*,  $C_6H_{11}\cdot NO_2$ , prepared by heating the hydrocarbon with nitric acid (sp. gr. = 1.075) at  $115$ — $120^{\circ}$  during 10 hours, is a pale yellow liquid having an odour resembling that of nitrobenzene; when rapidly distilled under diminished pressure, it is colourless. The substance boils at  $109^{\circ}$  and  $205.5$ — $206^{\circ}$  under pressures of 40 mm. and 768 mm. respectively; it has a sp. gr. = 1.0759 at  $0^{\circ}/0^{\circ}$ , and 1.0616 at  $20^{\circ}/20^{\circ}$ . Sodium ethoxide precipitates the *sodium* derivative in leaflets readily soluble in water; the solution develops an intense, reddish-brown coloration with ferric chloride, and yields, with lead acetate, a white precipitate which dissolves in excess of the agent.

The compound  $C_{12}H_{20}(NO_2)_2$  remains in the distilling flask when crude nitrohexanaphthene is fractionated, and crystallises from light petroleum in white, lustrous plates; it decomposes when gradually heated, but if plunged into liquid at  $200^{\circ}$ , melts at  $208$ — $209^{\circ}$ .

*Hexanaphthene ketone* (ketoexamethylene),  $C_6H_{10}O$ , prepared by heating nitrohexanaphthene with zinc dust and glacial acetic acid, is identical with the ketone obtained from hydroxyhexamethylene by von Baeyer (*loc. cit.*, 175), and yields adipic acid on oxidation. When the ketone, dissolved in a mixture of alcohol and ether, is reduced

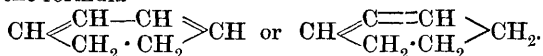
with sodium, *naphthenol* or *hexanaphthenol* (hydroxyhexamethylene) is produced.

*O-Naphtheneglycol*,  $C_6H_{10}(OH)_2$ , obtained by the action of potassium permanganate on naphthylene, crystallises from ethylic acetate in lustrous scales, and melts at  $99-100^\circ$ ; it sublimes slowly at  $70^\circ$ , and boils at  $225^\circ$  (uncorr.), when it undergoes partial decomposition.

*Amidonaphthene* or *amidohexanaphthene* (hexamethyleneamine),  $C_6H_{11}\cdot NH_2$ , a colourless liquid with a powerful odour of ammonia, is prepared by reducing nitrohexanaphthene with tin and hydrochloric acid; it boils at  $134^\circ$  under a pressure of 768 mm., and has the sp. gr. = 0.88216 at  $0^\circ/0^\circ$ , and 0.86478 at  $20^\circ/0^\circ$ . Derivatives of this base have been already described by von Baeyer (*loc. cit.*). The *hydrobromide* crystallises in elongated prisms, and yields a *platino-bromide* and an *auribromide*. The *hydriodide*, *nitrate*, and *oxalate* crystallise in needles, and the *sulphate* forms leaflets.

*Naphthylene* or *hexanaphthylene* (*tetrahydrobenzene*, *cyclohexene*) prepared from the chloride by the action of quinoline or of alcoholic potash, boils at  $83-84^\circ$  under a pressure of 752 mm., and has a sp. gr. = 0.80893 at  $0^\circ/0^\circ$ . The *dichloride*,  $C_6H_{10}Cl_2$ , boils at  $187-189^\circ$ .

The *hexaterpene*,  $C_6H_8$ , obtained from a hexanaphthylene dichloride which boils at  $190-192^\circ$ , has the penetrating odour of allylene, and is probably identical with von Baeyer's dihydrobenzene; it boils at  $83-86^\circ$  under a pressure of 767 mm., and has a sp. gr. = 0.8706 at  $0^\circ/0^\circ$ , and 0.8531 at  $20^\circ/0^\circ$ . One drop of the hydrocarbon develops an intense red coloration with a mixture of alcohol and concentrated sulphuric acid; the dibromide melts at  $184^\circ$ . An isomeric *hexaterpene*, prepared from the dichloride which boils at  $196-198^\circ$ , closely resembles the foregoing hydrocarbon; it boils at  $83-86^\circ$  under a pressure of 757 mm., and develops a deep violet-blue coloration with alcoholic sulphuric acid. Bromine converts it into an oily mixture, from which the dibromide melting at  $184^\circ$  crystallises. It is probable that this terpene has the constitution represented by the formula  $CH_2<\begin{smallmatrix} CH:CH \\ CH:CH \end{smallmatrix}>CH_2$ , whilst the terpene which develops a red coloration has the unsymmetrical constitution represented by the formula



Examination of the crystalline dibromide has shown it to be a mixture, fractions having been obtained, on recrystallisation, melting variously between  $184^\circ$  and  $192^\circ$ .

Hexanaphthene is converted almost quantitatively into adipic acid when it is heated with nitric acid of sp. gr. = 1.235 in sealed tubes in a water bath; the hydrocarbon obtained from naphtha is an advantageous source of the acid. Iodonaphthene and chloronaphthene are converted into methylpentamethylene when heated with hydriodic acid, a small quantity of hexamethylene being also produced (compare Abstr., 1897, i, 402).

A useful summary of the general properties of hexanaphthene and its derivatives brings the paper to a conclusion. M. O. F.

**Stereoisomeric Oximes in the Hydroaromatic Series.** By EMIL KNOEVENAGEL and J. GOLDSMITH (*Ber.*, 1898, 31, 2465—2474).—The oxime of 3-phenyl-1-methylcyclohexenone-5 has been obtained by Werner (*Dissertation Heidelberg*, 1894), and by Bialon (*ibid.*, 1897), who describe it as melting at  $115^{\circ}$ ; on the other hand, Jackson (*ibid.*, 1896) and Ruschhaupt (*ibid.*, 1897) obtained melting points of  $151^{\circ}$  and  $152^{\circ}$  respectively. Experiments made by the present authors show that the apparent discrepancy is due to the existence of two isomeric oximes, and that the character of the product obtained depends on the mode of preparation. The two substances may be separated, when admixed, by treatment with a mixture of alcohol and light petroleum in which the  $\alpha$ -oxime (m. p.  $115^{\circ}$ ) is much more readily soluble than the  $\beta$ -oxime (m. p.  $151^{\circ}$ ). The crude product is obtained by the method of Werner or of Ruschhaupt, according as it is desired that a predominance of the  $\alpha$ - or the  $\beta$ -modification respectively shall be produced. The former method consists in heating the ketone with a 10 per cent. solution of hydroxylamine hydrochloride in dilute alcohol on the water bath for an hour and a half; in the latter method, the ketone is dissolved in alcohol, mixed with an aqueous solution of sodium carbonate in excess, and then with solid hydroxylamine hydrochloride, the alcohol being finally driven off on the water-bath.

Both oximes are optically inactive. The  $\beta$ -oxime crystallises in the tetragonal system, the axial ratio being 1 : 0.6706.

The  $\alpha$ -derivative is converted into the  $\beta$ -modification when its solution in warm acetic acid is evaporated under slightly reduced pressure; the reverse change is effected by dissolving the  $\beta$ -oxime in warm soda and reprecipitating it from the solution by neutralisation, and the same result may be achieved by careful sublimation of the  $\beta$ -oxime.

Both oximes yield the original ketone on hydrolysis with dilute sulphuric acid, and, on reduction with sodium and alcohol, yield the same 5-amido-3-phenyl-1-methylcyclohexane (compare Jackson, *loc. cit.*). The *hydrochloride* of this base separates from hot water in crystals melting at  $235^{\circ}$ , and dissolves in chloroform and alcohol, but is insoluble in ether and light petroleum. The *platinochloride* has the composition  $(C_{13}H_{17}N), H_2PtCl_6$ .

Experiments were made with a view of ascertaining if the ketone suffered any change under the influence of small quantities of alkali or acid, but without noteworthy result, and the authors conclude that the relationship between the two oximes is a stereoisomeric one. It is uncertain as yet, however, which of them is the *cis* and which the *trans* form, although a possible clue to the question is afforded by the behaviour of the two oximes towards phosphorus pentachloride, as only the  $\beta$ -oxime yields any product having the properties of a nitrile.

Phenylmethylcyclohexenone yields two stereoisomeric *semicarbazones*, which may be separated by means of alcohol. One of these, the more sparingly soluble, melts at  $199$ — $200^{\circ}$  but has not as yet been analysed; the other is obtained in the form of bundles of white needles melting at  $170$ — $171^{\circ}$ , and has the composition  $C_{14}H_{17}NO_3$ .

A. I.

**Formation of Suberone from Ecgonine.** By RICHARD WILLSTÄTTER (*Ber.*, 1898, 31, 2498—2508. Compare *Abstr.*, 1893, i, 378, 713; 1894, i, 523).—Hydrotropilidinecarboxylic acid, prepared by the methylation of hydroecgonidine ethylic ether, is converted by reduction with sodium and amyl alcohol into cycloheptanecarboxylic acid,  $C_7H_{13} \cdot COOH$ , which is identical with the acid obtained by Einhorn and Willstätter by the reduction of tropilidinecarboxylic acid. This acid readily yields a monobromo-derivative, which, on treatment with baryta, is converted into Spiegel's  $\alpha$ -hydroxycycloheptanecarboxylic acid,  $OH \cdot C_7H_{12} \cdot COOH$  (*Trans.*, 1881, 541),  $\Delta^1$ -cycloheptenecarboxylic acid,  $C_7H_{11} \cdot COOH$ , being produced at the same time; the latter melts at  $49-50^\circ$ , and is identical with the  $\Delta^1$ -ethylcyclopentenecarboxylic acid of Einhorn and Willstätter; this also has been prepared by Spiegel, and by Buchner and Jacobi (*Abstr.*, 1898, i, 637). When  $\alpha$ -hydroxycycloheptanecarboxylic acid is treated with lead peroxide, it is at once converted into suberone, 40 per cent. of the theoretical yield being obtained.

It thus appears that the acid,  $C_7H_{13} \cdot COOH$ , which melts at  $245-248^\circ$  and yields an amide melting at  $195^\circ$ , and was described as 1:4-ethylcyclopentanecarboxylic acid by Einhorn and Willstätter, is identical with Spiegel's cycloheptanecarboxylic acid.

The three ethylcyclopentenecarboxylic acids are in reality cycloheptenecarboxylic acids, the one melting at  $50^\circ$  being identical with Spiegel's suberenecarboxylic acid.

Hydrotropilidinecarboxylic acid is a cycloheptadienecarboxylic acid in which the position of the ethylene linkings is unknown.

Finally, the three paramethylenedihydrobenzoic acids or tropilidinecarboxylic acids are cycloheptatrienecarboxylic acids, whilst Buchner's  $\alpha$ -isophenylacetic acid (*Abstr.*, 1898, i, 639) is the fourth possible isomeride.

These facts, moreover, render it extremely probable that tropilidine itself is cycloheptatriene, whilst hydrotropilidine is cycloheptadiene.

A. H.

**Interchange of Halogens in the Aromatic Series.** By VICTOR THOMAS (*Compt. rend.*, 1898, 127, 184—186).—When 1:4-dibromobenzene is heated in a reflux apparatus with from ten to twelve times its weight of anhydrous ferric chloride, there is abundant evolution of hydrogen chloride, and the principal product of the reaction is penta-chlorobromobenzene,  $C_6Cl_5Br$ , which crystallises in long needles melting at  $228^\circ$ . In this reaction, the ferric chloride effects the displacement of 1 atom of bromine in the dibromobenzene by chlorine, an interchange which is common in the aliphatic, but rare in the aromatic, series. The bromine is not evolved as hydrogen bromide, but enters into combination with the iron to form a bromide or, perhaps, a chlorobromide. Whether the displacement of bromine by chlorine follows or precedes the further chlorination of the dibromobenzene, is a problem which the author hopes to solve by a study of the bye-products of the reaction. These are formed in very small quantity, and consist of a white substance melting at about  $20^\circ$ , and a compound crystallising in needles, melting at  $120^\circ$ , and readily subliming. N. L.

**Pyrogenic Decomposition of Gas-oil, Phenol, and Cresol.**  
By E. MÜLLER (*J. pr. Chem.*, 1898, 58, [ii], 1—50).—The substance to be decomposed was allowed to flow into an iron tube, 120 cm. long by 1.3 cm. wide, placed in a combustion furnace and tilted slightly downwards; a length of 65 cm. was heated in the furnace by means of direct flames, the last half to 700—800°, the first half to a rather lower temperature; the ends of the tube surrounding the india-rubber bungs were jacketed with a current of cold water. The products of decomposition were passed first through a distillation flask of 150 c.c. capacity kept cool with ice and salt, and then through a tower, 5 cm. wide by 30 cm. high, fitted with 24 horizontal plates, each bored with a few holes in such a way that the holes in one plate were never directly above those in the plate below: the tar condensed in the flask, and in the tower smoky matter was deposited. After leaving the tower, the gas, now colourless, passed a Winkler's spiral washing apparatus and two wash bottles, all filled with petroleum; after this, it was collected in the gasometer, which consisted of two large glass carboys of some 60 L. capacity containing water. In some cases, three wash bottles containing ammoniacal silver nitrate and then two containing sulphuric acid were inserted between the tower and the petroleum absorption vessels; in them, the acetylene was absorbed, and it was estimated by filtering off the impure silver acetylide, decomposing it with hydrochloric acid, dissolving out the silver chloride with ammonia, reprecipitating and weighing it; the amount of acetylene was always very small. The benzene formed was determined by distilling the tar and contents of the petroleum absorption vessels, collecting what came over below 120°, nitrating this, distilling the nitrobenzene over with steam, extracting it from the distillate with ether, and weighing; more benzene condensed in the tar than passed on with the gas. By dissolving the residual tar in chloroform and precipitating with light petroleum, the solid hydrocarbons, including naphthalene, could be isolated. The density of the moist gas obtained was compared with that of moist air by observing the rates of flow of the two gases through a capillary orifice; the density of the gas when dry was then calculated. Finally, a residue of solid carbon was left in the iron tube.

The table on page 28 gives the results of the experiments.

The experiment with gas oil was made for purposes of comparison; the gas contained much ethylene and had a good illuminating power, and practically no carbon was left in the tube. With phenol, the volume of gas obtained was nearly as great, but it contained little ethylene and had practically no illuminating power, and there was a large amount of soot formed; from the composition of the gas, it would seem that the bulk of the phenol decomposes according to the equation  $C_6H_6O = CO + 3H_2 + 5C$ . With cresol, the results were similar, except that more methane and benzene were produced, and the gas had a feeble illuminating power; the decomposition appears to take place largely according to the equation  $CH_3 \cdot C_6H_4 \cdot OH = CO + CH_4 + 2H_2 + 5C$ . In two experiments, when the cresol was fed in rather more quickly, and as a consequence the temperature in the iron tube somewhat reduced, a very large quantity of tar was obtained with a smaller quantity of gas, and but little coke remained in the tube. With

Quantities given are per 100 grams of material used.		Gas oil.	Phenol.	Cresol.	Gas oil and phenol.	Gas oil and cresol.	Oil of turpentine b. p. 155—160°.
Material used	per {grams.	0.5	0.44	0.20	0.34	0.52	0.23
Gas evolved	{ minute, { c.c.	240	282	132	132	240	126
Gas obtained (at 0° and 760 mm.)	litres.	44.68	64.81	60.30	39.75	46.00	60.01
1 litre of dry gas weighed,	grams	1.012	0.562	0.600	0.736	0.815	0.629
Composition of gas :—							
Ethylene.....	grams	27.6	1.05	1.1	9.7	10.8	6.7
Carbonic oxide.....	,,	0.9	24.9	21.9	7.3	9.6	2.5
Hydrogen.....	,,	0.3	3.4	2.7	1.2	1.0	1.7
Methane.....	,,	15.2	4.1	8.2	9.6	12.9	23.8
Distillate below 120°:							
Weight.....	grams	12.8	7.8	16.6	8.0	17.0	15.0
Sp. gr.....		0.801	0.910	0.899	0.910	0.903	0.888
Benzene.....	grams	5.8	4.4	10.5	5.2	8.5	6.0
Percentage yield :—							
Gas.....		44	33.5	34	27.5	34	34.5
Carbon.....		—	29	28	2	0.5	1.5
Tar and petroleum absorp- tion.....		51.5	28	32	64	59	52
Loss.....		4.5	9.5	6	6.5	6.5	12

mixtures of gas oil with either phenol or cresol in equal proportions, both parts of the mixture undergo decomposition, and the gas, as regards composition and illuminating power, stands between those obtained with the pure constituents; there is practically no formation of coke, however. If the temperature is reduced a little below 700°, by feeding in the material faster, only the gas oil undergoes decomposition; the phenol distils over unchanged and is collected with the tar. With oil of turpentine, which contains several methyl groups, the amount of methane present in the gas is very large.

C. F. B.

Constitution of the Nitramidophenol which is produced by the action of Sulphuric Acid on Orthonitrodiazobenzene-imide. By FRIEDRICH KEHRMANN and ERNST GAUHE (*Ber.*, 1898, 31, 2403—2405. Compare *Abstr.*, 1898, i, 45, and this vol., i, 31).—The nitramidophenol prepared from orthonitrodiazobenzene-imide by the action of sulphuric acid is converted by reduction into 4-hydroxy-orthophenylenediamine,  $C_6H_3(NH_2)_2 \cdot OH$ , the hydrochloride of which crystallises in thick, almost colourless tablets. The triacetyl derivative of this base crystallises in colourless needles, melts at 184—185°, and is converted by dilute aqueous soda into diacetamidophenol,  $OH \cdot C_6H_3 \cdot (NHAc)_2$ , which crystallises in prisms melting at 205—207°. This substance is converted by oxidation into acetamidoquinone, the formation of which proves the constitution of the foregoing compounds.

A. H.

**General Method for the Preparation of Mixed Carbonates of the Fatty and Aromatic Series.** By PAUL CAZENEUVE and ALBERT MOREL (*Compt. rend.*, 1898, 126, 1871—1873).—Mixed carbonates of the fatty and aromatic series are readily obtained by heating normal phenylic carbonate or its homologues with the alcohols of the fatty series in presence of certain organic bases, such as carbamide. In this way, phenylic alkylic carbonates have been prepared containing methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, and allyl. With the alcohols of higher molecular weight, some allophanates and urethanes are formed, but these secondary products can be avoided by using aniline, dimethylaniline, pyridine, quinoline, and some other bases in place of carbamide. Mixed alkylic carbonates of guaiacol, thymol, and tolyl were prepared in the same way.

In the absence of a base, little or no reaction takes place. Most probably the bases first form alcoholates which afterwards react in this manner,  $\text{CO}(\text{OPh})_2 + \text{C}_5\text{NH}_5 \cdot \text{EtOH} = \text{OEt} \cdot \text{CO} \cdot \text{OPh} + \text{C}_5\text{NH}_5 \cdot \text{PhOH}$ .

When sodium ethoxide, dissolved in alcohol, is added to a well cooled solution of phenylic carbonate in ether-alcohol, phenylic ethylic carbonate is obtained in considerable quantity. In several cases, this reaction affords a better method of preparing the mixed carbonates than the other reaction just described.

C. H. B.

**Mixed Phenylic Alkylic Carbonates.** By PAUL CAZENEUVE and ALBERT MOREL (*Compt. rend.*, 1898, 127, 111—113).—The following mixed ethereal carbonates have been prepared by the general method indicated by the authors in a previous communication (compare preceding abstract).

*Phenylic methylic carbonate*, obtained by heating phenylic carbonate and carbamide in excess of methylic alcohol, boils at 190—200° under a pressure of 754 mm., and at 123° under 44 mm.; its sp. gr. = 1.1607 at 0°.

*Phenylic propylic carbonate* boils at 210—220° (750 mm.), and at 120—130° (30 mm.); its sp. gr. = 1.0756 at 0°.

*Phenylic isopropylic carbonate* boils at 220° (750 mm.), and at 141—142° (70 mm.).

*Phenylic isobutylic carbonate*, obtained by heating phenylic carbonate and isobutylic alcohol with pyridine, boils at 220—225° (750 mm.), and at 130° (30 mm.); its sp. gr. = 0.9941 at 0°.

*Phenylic isoamylic carbonate*, produced like the preceding compound, boils at 220° (760 mm.), and at 120—130° (60 mm.); its sp. gr. = 1.0 at 0°.

These mixed carbonates are all colourless liquids with an agreeable odour and are miscible with the usual organic solvents.

*Phenylic allylic carbonate*, which is a colourless liquid with an alliaceous odour, boils at 130° under a pressure of 70 mm. G. T. M.

**Action of Bromine on 1:4-Tertiary Butylphenol in Presence of Aluminium Bromide.** By F. BODROUX (*Compt. rend.*, 1898, 127, 186—188).—1:4-Tertiary butylphenol,  $\text{CMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , reacts vigorously with bromine in the presence of aluminium bromide, with the formation of a substance which analysis shows to be pentabromophenol. As a general rule, when monhydric phenols are treated

with bromine in the presence of aluminium bromide, the maximum substitution occurs in the benzene nucleus. A side chain attached to the nucleus through a C or CH group is destroyed, and an atom of bromine takes its place. If, on the other hand, the linking is effected by a  $\text{CH}_2$  group, the side chain remains unaffected. N. L.

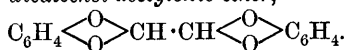
**Nitration and Oxidation Products of Phenols which are Insoluble in Alkalis.** By KARL AUWERS and F. RAPP (*Annalen*, 1898, 302, 153—171. Compare Auwers, Abstr., 1897, i, 336).—The compound,  $\text{C}_8\text{H}_6\text{Br}_3\text{NO}_3$ , obtained by the action of fuming nitric acid on tribromortho-xlenol, separates from petroleum in small, lustrous crystals, and melts at  $97-99^\circ$ ; the compound from tribromopara-xlenol melts at  $85-86^\circ$ . The compound,  $\text{C}_9\text{H}_5\text{Br}_2\text{NO}_3$ , from dibromomesitol, forms hexagonal crystals, and melts at  $72^\circ$ .

The compound,  $\text{C}_8\text{H}_7\text{Br}_3\text{O}_2$ , produced on heating a glacial acetic acid solution of the nitro-compound from tribromortho-xlenol, crystallises in long prisms, and melts at  $178-180^\circ$ ; dibromopara-xyloquinone is formed when the nitro-compound from tribromopara-xlenol is treated in the same way, whilst the nitro-compound from dibromomesitol yields the compound,  $\text{C}_9\text{H}_{10}\text{Br}_2\text{O}_2$ , which crystallises from petroleum in lustrous prisms, and melts at  $132^\circ$ .

It has been pointed out (*loc. cit.*) that, when heated in glacial acetic acid, the nitro-compound from dibromo- $\psi$ -cumenol yields the compound  $\text{C}_9\text{H}_{10}\text{Br}_2\text{O}_2$ , which is identical with the substance obtained by Zincke from dibromo- $\psi$ -cumenol under the influence of dilute nitric acid (Abstr., 1896, i, 214); the *acetyl* and *diacetyl* derivatives melt at  $95-96^\circ$  and  $102-103^\circ$  respectively. Hydrogen chloride is without action on the substance, but in presence of zinc chloride converts it into the chloride of dibromanhydroparahydroxy- $\psi$ -cumyl alcohol which melts at  $110^\circ$ ; the same compound is produced by the action of phosphorus pentachloride, whilst hydrogen bromide and phosphorus pentabromide give rise to dibromo- $\psi$ -cumenol.

The constitution of the nitro-compounds is discussed in the original paper. M. O. F.

**Ethanedicathechol [Dicathechol Acetylenic Ether].** By CHARLES MOUREU (*Compt. rend.*, 1898, 127, 69—71. Compare Abstr., 1898, 644).—Acetylene dibromide interacts violently with a solution of catechol in aqueous or alcoholic potash; spontaneously inflammable monobromacetylene is evolved, whilst catechol acetylenic ether, the normal and expected product of the reaction, appears not to be formed. With acetylene tetrabromide, on the contrary, a definite condensation product is formed, which may be separated by steam distillation from the other products of the reaction; this compound crystallises from alcohol in thin leaves melting at  $88-89^\circ$ , and is shown by analysis, and by a cryoscopic determination of its molecular weight (found, 235; theory, 242) to have the formula  $\text{C}_{14}\text{H}_{10}\text{O}_4$ , corresponding with *dicathechol acetylenic ether*,

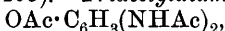


On hydrolysis with dilute sulphuric acid, it yields catechol and a substance which, after purification, crystallises in white, nacreous leaves

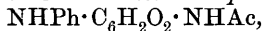


melting at 130—131°, and is shown by analysis, and by an ebullioscopic molecular weight determination (found, 160; theory, 168) to have the formula  $C_8H_8O_4$ . This compound, the constitution of which will be discussed hereafter, is slightly soluble in cold water, and readily in hot water, alkalis, and organic solvents; the aqueous solution reduces an ammoniacal solution of silver nitrate, and gives an intense blue coloration with ferric chloride. N. I.

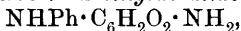
**Amidoquinone.** By FRIEDRICH KEHRMANN and GABRIEL BAHATRIAN (*Ber.*, 1898, 31, 2399—2403).—*Triacetyldiamidophenol*,



obtained by the action of acetic anhydride and sodium acetate on diamidophenol, crystallises in colourless needles and melts at 180—182°. When it is dissolved in dilute aqueous soda and the solution acidified, the precipitate consists of *diacetamidophenol*,  $OH \cdot C_6H_3(NHAc)_2$ , which crystallises in colourless needles melting at 220—222°, and is converted by oxidation with sodium dichromate and sulphuric acid into *acetamidoquinone*,  $C_6H_3O_2 \cdot NHAc$ ; the latter crystallises in reddish-yellow, thick prisms melting at 142°. It has been found impossible to convert this compound into amidoquinone. *Acetamidophenol*,  $NHAc \cdot C_6H_3(OH)_2$ , obtained by reducing the foregoing compound with sulphurous acid, forms greyish-white, granular crystals melting at 100°. *Anilidoacetamidoquinone*,



obtained on adding aniline to an alcoholic solution of acetamidoquinone, crystallises in almost black, glistening needles which melt and decompose at 278—280°. *Phenyldiamidoquinone*,



obtained by the reduction of the anilido-compound with stannous chloride and hydrochloric acid, crystallises in violet-brown plates melting at 280—282°. When it is heated with dilute aqueous soda, it is converted into 1:4-dihydroxyquinone and *anilidohydroxyquinone*,  $NHPh \cdot C_6H_2O_2 \cdot OH$ ; the latter crystallises in plates having a violet surface-lustre, and melting and decomposing at 228—230°. The formation of 1:4-dihydroxyquinone by the action of alkalis on this compound and on phenyldiamidoquinone, proves the constitution of anilidoacetamidoquinone. When acetamidoquinone is treated with concentrated hydrochloric acid, it is converted into *chloracetamidophenol*, and this, on oxidation with chromic acid, passes into *chloracetamidoquinone*,  $C_6H_2ClO_2 \cdot NHAc$ ; the latter crystallises in golden-yellow prisms melting at 174—175°, and is converted by aniline into anilidoacetamidoquinone. The corresponding bromine compound crystallises in large, golden-yellow plates melting at 183—185°. A. H.

**Condensation Products of Phloroglucinol and of Phloroglucide.** By JOSEF HERZIG (*Monatsh.*, 1898, 19, 376—383).—When triacetylphloroglucinol is hydrolysed with sulphuric acid, in order to determine the number of acetyl groups present, a yellow condensation product is obtained when the acid is of a certain strength. If the acetyl derivative is heated for an hour on the water bath with a mixture of equal volumes of sulphuric acid and water, the theoretical yield of acetic acid is obtained, and none of the yellow compound is

formed. By the use of a stronger acid and of a higher temperature, less than the theoretical amount of acetic acid is obtained, namely, 5 molecules from 2 of the acetyl derivative, and the yellow condensation product is also formed. The best results are obtained at a temperature of 130—140°, and with an acid containing 2 volumes of sulphuric acid to 1 of water. These results indicate that 1 molecule of acetic acid is employed in condensing 2 molecules of phloroglucinol to the yellow compound.

*Acetylphloroglucinol diethyl ether*,  $C_6H_3(OEt)_2 \cdot OAc$ , crystallises from hot alcohol in long, colourless needles melting at 54—55°. When heated on the water bath with equal volumes of sulphuric acid and water, the theoretical amount of acetic acid is obtained (namely, 1 molecule), but when heated with two volumes of acid and one of water at 130—140°, only half the theoretical yield of acetic acid is obtained, and a yellow condensation product is also formed. Similar results are given with acetylphloroglucinol monethyl ether. These condensation products are probably to be regarded as anhydrides; when hydrolysed with alkalis, they yield, not phloroglucinol, but a substance which is probably phloroglucide. With acetylphloroglucide,  $C_{12}H_5(OAc)_5$ , it is found that a condensation product is formed from 1 molecule of acetic acid and 1 of the phloroglucide. J. J. S.

**Homologous Phloroglucinols from Filicic Acid and from Aspidin.** By RUDOLF BOEHM (*Annalen*, 1898, 302, 171—191. Compare Weidel, Abstr., 1898, i, 578).—By heating filicic acid with zinc dust and 15 per cent. caustic soda on a water bath during 8 hours, phloroglucinol, methylphloroglucinol, dimethylphloroglucinol, and trimethylglucinol are produced; aspidin, when heated with caustic soda in a silver dish, yields filicic acid and the methyl ether of methylphloroglucinol.

*Dibromomethylphloroglucinol*,  $C_7H_6Br_2O_3$ , prepared by adding bromine to a solution of the phenol in glacial acetic acid, crystallises from dilute alcohol in elongated, thin prisms containing  $3H_2O$ , and melts indefinitely at 120—125°; it becomes anhydrous at 100°, and in this condition melts at 137° when slowly heated. *Tribenzoylmethylphloroglucinol* crystallises from alcohol in colourless prisms, and melts at 111—112°; *benzeneazomethylphloroglucinolazobenzene* forms beautiful, red needles, and melts at 236—237°.

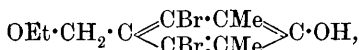
*Tribromotrimethylphloroglucinol*,  $C_9H_{11}Br_3O_3$ , crystallises from alcohol in colourless, six-sided prisms and melts at 88—90°. M. O. F.

**Anhydroparahydroxymesitylic Alcohol and its Products of Change.** By KARL AUWERS and H. ALLENDORFF (*Annalen*, 1898, 302, 76—98. Compare Abstr., 1898, i, 646).—The bromide of dibrom-

anhydroparahydroxymesitylic alcohol,  $CBr \begin{array}{c} \diagup CBr:CM_e \\ CH_2 - O \\ \diagdown CBr:CM_e \end{array} CH$ , prepared

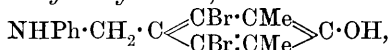
by the action of bromine dissolved in glacial acetic acid on mesitol, crystallises in elongated, lustrous needles, and melts at 146—147°; phenylic cyanate in benzene at 100° converts it into the compound  $C_{16}H_{14}Br_3NO_2$ , which melts at 226°.

*Dibromoparahydroxymesitylic ethylic ether*,



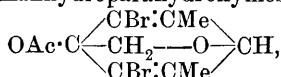
obtained on treating the bromide with boiling absolute alcohol, crystallises from petroleum in lustrous, white prisms, and melts at  $147^\circ$ . The *acetyl* derivative separates in lustrous needles, and melts at  $88^\circ$ .

*Dibromoparahydroxymesitylaniline*,

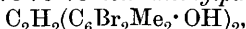


produced by the action of aniline, dissolved in benzene, on the bromide, crystallises from alcohol in yellowish, flattened prisms, and melts at  $136$ – $137^\circ$ ; the *phenylurethane* separates from benzene in white needles, and melts at  $183^\circ$ . *Dibromoparahydroxymesitylpiperidine*, prepared in a similar manner from piperidine, crystallises from alcohol in prisms melting at  $134^\circ$ ; the *acetyl* derivative forms lustrous, white needles, and melts at  $122$ – $123^\circ$ .

The *acetate* of dibromanhydroparahydroxymesitylic alcohol,

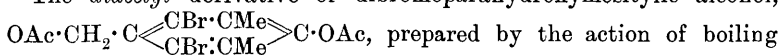


obtained by adding sodium acetate (1 mol.) to a solution of the bromide in hot acetic acid, crystallises from benzene in small, lustrous prisms, and melts at  $165$ – $166^\circ$ . Cold caustic soda converts it into 2 : 6 : 2' : 6'-*tetrabromo-3 : 5 : 3' : 5'-tetramethylparadihydroxystilbene*,



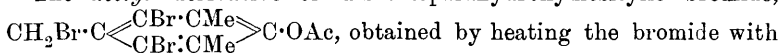
which crystallises from benzene in small needles, and melts at  $232^\circ$  when heated rapidly; the *diacetyl* derivative forms white needles and melts at  $244^\circ$ .

The *diacetyl* derivative of dibromoparahydroxymesitylic alcohol,

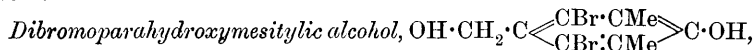


prepared by the action of boiling acetic anhydride on the acetate of dibromanhydroparahydroxymesitylic alcohol during 2 hours, crystallises in lustrous, white needles, and melts at  $159$ – $160^\circ$ ; hydrogen bromide acting on the substance dissolved in glacial acetic acid regenerates the bromide (m. p.  $146$ – $147^\circ$ ).

The *acetyl* derivative of dibromoparahydroxymesitylic bromide,



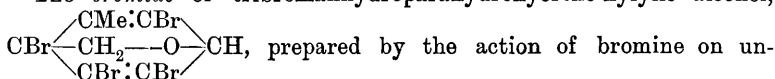
obtained by heating the bromide with acetic anhydride during several hours, crystallises in beautiful, long needles, several centimetres in length, and melts at  $150$ – $151^\circ$ . Alcoholic potash converts it into dibromoparahydroxymesitylic ethylic ether, which is also produced by the action of alcohol in sealed tubes at  $100^\circ$ ; silver oxide gives rise to the *diacetyl* derivative of tetrabromoparadihydroxymesitylic ether,  $\text{O}(\text{CH}_2 \cdot \text{C}_6\text{Br}_2\text{Me}_2 \cdot \text{OAc})_2$ , which crystallises in white needles and melts at  $228$ – $229^\circ$ . The compound,  $\text{C}_{22}\text{H}_{20}\text{Br}_4\text{O}_4$ , is obtained by the action of alcoholic sodium ethoxide (1 mol.) on the acetyl derivative of dibromoparahydroxymesitylic bromide; it melts at  $217$ – $218^\circ$ . The *isobutyryl* derivative of dibromoparahydroxymesitylic bromide crystallises from alcohol in lustrous needles and melts at  $152$ – $154^\circ$ .



is obtained by heating the bromide of dibromanhydroparahydroxy-mesitylic alcohol with aqueous acetone in a reflux apparatus, the crystalline product being extracted with glacial acetic acid, in which a less readily fusible bye-product remains undissolved; it melts at 191—192° when heated rapidly, but if the temperature rises slowly, the substance forms a turbid liquid at 188°, subsequently solidifies, and finally melts at 240—250°. This is due to its conversion into an isomeric *compound* which melts at 252°, and is transformed into the alcohol when the solution in benzene or xylene is boiled. Hot acetic anhydride converts the alcohol into the acetyl derivative of dibromanhydroparahydroxymesitylic alcohol.

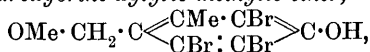
M. O. F.

**Derivatives of Anhydroparahydroxyortho-xylic Alcohol, and of Anhydro-orthohydroxypseudocumylic Alcohol.** By KARL AUWERS and H. VAN DE ROVAART (*Annalen*, 1898, 302, 99—107). —The bromide of tribromanhydroparahydroxyortho-xylic alcohol,



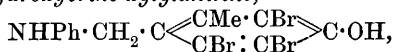
symmetrical ortho-xylene, crystallises from boiling glacial acetic acid in lustrous needles, and melts at 171—173°.

*Tribromoparahydroxyortho-xylic methylic ether,*



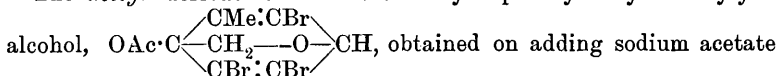
formed when the bromide is treated with boiling methylic alcohol, crystallises from petroleum in silky needles, and melts at 122—123°.

*Tribromoparahydroxyortho-xylicaniline,*



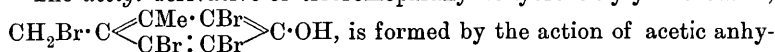
produced on adding a solution of aniline (2 mols.) in benzene to the bromide, melts somewhat indefinitely at 120—125°. *Tribromoparahydroxyortho-xylicpiperidine*, crystallises in reddish needles, and melts at 155—158°.

The *acetyl* derivative of tribromanhydroparahydroxyortho-xylic



(1 mol.) to a solution of the bromide in hot acetic acid, crystallises from benzene in small, white needles, and melts at 142—143°.

The *acetyl* derivative of tribromoparahydroxyortho-xylic bromide,

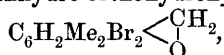


dride on the bromide of tribromanhydroparahydroxyortho-xylic alcohol, and crystallises from glacial acetic acid in small, lustrous needles; it melts at 138—140°, and is indifferent towards hot, aqueous alkalis.

*Orthohydroxy-ψ-cumylic alcohol*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , is prepared by treating a solution of ortho-xylene in caustic soda with aqueous formaldehyde; after an interval of 2 days, the liquid is nearly neutralised with acetic acid, and saturated with carbonic anhydride, which precipitates the hydroxy-alcohol. It crystallises from

xylene in nacreous leaflets and needles melting indefinitely at 108—114°.

The *bromide* of bromanhydro-orthohydroxy- $\psi$ -cumylic alcohol,

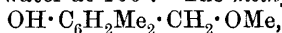


formed on adding bromine in glacial acetic acid to a solution of the hydroxy-alcohol in the same medium, crystallises from light petroleum in needles, and melts at 66—67°.

M. O. F.

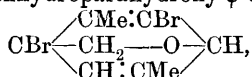
**Parahydroxypseudocumylic Alcohol and its Products of Bromination.** By KARL AUWERS and H. ERCKLENTZ (*Annalen*, 1898, 302, 107—130. Compare Auwers and Baum, *Abstr.*, 1897, i, 34).—*Dibromopara-xyleneol*,  $[\text{Me}_2 : \text{Br}_2 : \text{OH} = 1 : 4 : 2 : 5 : 6]$ , is prepared by adding bromine (2 mols.) dissolved in glacial acetic acid to para-xyleneol in the same medium, from which it crystallises in large, lustrous needles melting at 79°. The bromo- and tribromo-derivatives, which melt at 87° and 177—178° respectively, have been described by Jacobsen; the *benzoyl* derivative of tribromopara-xyleneol crystallises in small, white needles, and melts at 89—90°.

*Parahydroxy- $\psi$ -cumylic alcohol*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , prepared from para-xyleneol and formaldehyde (compare foregoing abstract), crystallises from ethylic acetate in lustrous, rhombic plates, melts at about 165°, and loses water at 160°. The *methylic ether*,



obtained on heating the substance with methylic alcohol at 150—160°, forms aggregates of lustrous needles, and melts at 101°. The *dimethylic ether*,  $\text{OMe} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , results from the action of methylic iodide and sodium methoxide; it melts at 88°, and boils at 129° under a pressure of 16.5 mm.

The *bromide* of bromanhydroparahydroxy- $\psi$ -cumylic alcohol,



obtained on adding a solution of bromine in chloroform to parahydroxy- $\psi$ -cumylic alcohol suspended in the same medium, crystallises from glacial acetic acid in long, lustrous needles, and melts at 81°. Bromine acts vigorously on the substance, converting it into the bromide of dibromanhydroparahydroxy- $\psi$ -cumylic alcohol; zinc and hydrochloric acid reduce it to bromo- $\psi$ -cumenol, which melts at 32°.

*Bromoparahydroxy- $\psi$ -cumylaniline*,

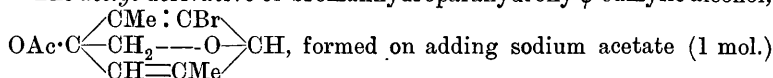


formed by the action of aniline on the bromide, crystallises from petroleum in leaflets, and melts at 75°. *Bromoparahydroxy- $\psi$ -cumyl piperidine* crystallises from alcohol in small needles, and melts at 81—82°.

*Bromoparahydroxy- $\psi$ -cumylic ether*,  $\text{O}(\text{CH}_2 \cdot \text{C}_6\text{HMe}_2\text{Br} \cdot \text{OH})_2$ , prepared by boiling the bromide with aqueous acetone, after crystallisation from boiling benzene, melts at 162°; concentrated sulphuric acid develops a carmine-red coloration. The *diacetyl* derivative separates

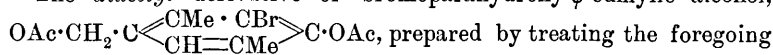
from glacial acetic acid in slender, lustrous needles, and melts at 140°. The *thio-ether*,  $\text{S} \cdot \text{C}_2\text{H}_4(\text{C}_6\text{HMe}_2\text{Br} \cdot \text{OH})_2$ , obtained on agitating the bromide with aqueous potassium sulphide, melts at 152°.

The *acetyl* derivative of bromanhydroparahydroxy- $\psi$ -cumylic alcohol,



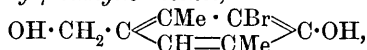
to a boiling solution of the bromide in glacial acetic acid, crystallises in lustrous needles and melts at 65°. The *chloride*,  $\text{C}_9\text{H}_{10}\text{BrClO}$ , is obtained on passing hydrogen chloride into a solution of the acetyl derivative in methylic alcohol, and melts at 73—74°; the *iodide* melts at 94°.

The *diacetyl* derivative of bromoparahydroxy- $\psi$ -cumylic alcohol,



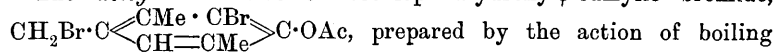
acetyl derivative with boiling acetic anhydride, crystallises from light petroleum in flattened prisms, and melts at 83—84°.

*Bromoparahydroxy- $\psi$ -cumylic alcohol*,



obtained on hydrolysing the diacetyl derivative with alcoholic potash, crystallises from petroleum in lustrous needles, and melts at 90—91°. Acetic chloride converts it into the acetyl derivative of bromanhydroparahydroxy- $\psi$ -cumylic alcohol (m. p. 65°).

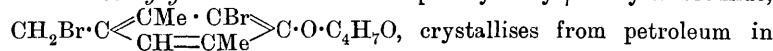
The *acetyl* derivative of bromoparahydroxy- $\psi$ -cumylic bromide,



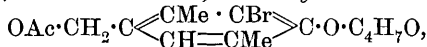
acetic anhydride on the bromide of bromanhydroparahydroxy- $\psi$ -cumylic alcohol (m. p. 81°), crystallises from petroleum in small, silky needles and melts at 92—93°. The *acetyl isobutyryl* derivative of bromopara-

hydroxy- $\psi$ -cumylic alcohol,  $\text{C}_4\text{H}_7\text{O} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{C} \begin{array}{c} \swarrow \text{CMe} \cdot \text{CBr} \\ \text{CH} = \text{CMe} \end{array} \text{C} \cdot \text{OAc}$ , obtained from the foregoing substance and silver isobutyrate, separates from its solution in light petroleum in lustrous, transparent prisms, and melts at 49—50°.

The *isobutyryl* derivative of bromoparahydroxy- $\psi$ -cumylic bromide,



lustrous needles, and melts at 91°; the *acetyl* derivative,



obtained from it by the action of silver acetate, crystallises from well cooled solutions in light petroleum, and melts at 39—40°.

M. O. F.

**Bromination Products of Saligenin.** By KARL AUWERS and G. BUTNER (*Annalen*, 1898, 302, 131—152).—According to the experimental conditions, the bromination of saligenin proceeds in three different directions. Treatment in aqueous solution with bromine water at the ordinary temperature gives rise to bromosaligenin and dibromosaligenin; at 50—60°, the same agent produces tribromo-

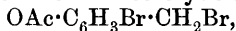
phenol, bromanil, and Benedikt's ketobromide, which probably has the constitution,  $\text{CBr} \begin{smallmatrix} \text{CH} \cdot \text{CBr}_2 \\ \text{CH} : \text{CBr} \end{smallmatrix} \text{CO}$  (Abstr., 1880, 246); finally, bromination in organic solvents yields the bromides of bromanhydrosaligenin and of dibromanhydrosaligenin. These bromides resemble those of the parahydroxy-alcohols and paramethylphenols in their behaviour towards alcohols, bases, water, organic anhydrides, and sodium acetate in presence of acetic anhydride; they are indifferent, however, to alkali sulphides, and yield compounds with sodium acetate in acetic acid which differ from those derived from the bromides hitherto described. Moreover, unlike the latter, the acetyl derivatives corresponding with them, and the piperidine derivatives, are not converted into derivatives of stilbene.

*Bromosaligenin*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}_2 \cdot \text{OH}$  [ $\text{CH}_2 \cdot \text{OH} : \text{Br} : \text{OH} = 1 : 2 : 5$ ], crystallises from benzene in large, lustrous leaflets, and melts at  $107-109^\circ$ ; unlike saligenin, it does not develop a red coloration with concentrated sulphuric acid, but ferric chloride produces a blue coloration in the aqueous solution.

*Dibromosaligenin* [ $\text{CH}_2 \cdot \text{OH} : \text{OH} : \text{Br}_2 = 1 : 2 : 3 : 5$ ] crystallises in long, white needles from a mixture of petroleum and benzene, and melts at  $88-89^\circ$ ; ferric chloride develops a violet-blue coloration in the aqueous solution, but concentrated sulphuric acid is without action on the substance.

The bromide of bromanhydrosaligenin,  $\text{C}_6\text{H}_4\text{Br}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$ , crystallises from benzene or petroleum in beautiful needles, and melts at  $98^\circ$ ; reduction with zinc and hydrochloric acid converts it into bromorthocresol, the action of aqueous acetone giving rise to bromosaligenin. *Bromorthocresylaniline*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}_2 \cdot \text{NHPh}$ , formed on adding a benzene solution of aniline to the bromide, crystallises from dilute alcohol in rhombohedra, and melts at  $114-115^\circ$ . *Bromorthocresylpiperidine* melts at  $63-64^\circ$ .

The acetyl derivative of bromorthocresylic bromide,

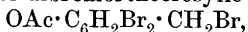


formed by the action of boiling acetic anhydride on the bromide of bromosaligenin, crystallises from alcohol in long, white needles, and melts at  $63-64^\circ$ . The acetyl derivative of bromosaligenin is produced if sodium acetate is present, and crystallises from petroleum in long, silky needles melting at  $100-101^\circ$ .

The bromide of dibromanhydrosaligenin,  $\text{C}_6\text{H}_3\text{Br}_3 \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$ , crystallises from glacial acetic acid in large, lustrous needles, and melts at  $116-118^\circ$ ; reduction converts it into 3:5-dibromorthocresol, and dibromosaligenin is obtained from it under the influence of boiling aqueous acetone.

*Dibromorthocresylic methylic ether*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OMe}$ , prepared from the bromide by the action of boiling methylic alcohol, forms a pale yellow oil. *Dibromorthocresylaniline*,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{NHPh}$ , crystallises from alcohol in needles, and melts at  $98-99^\circ$ , and *dibromorthocresylpiperidine* melts at  $99-100^\circ$ .

The *acetyl* derivative of dibromorthocresylic bromide,



separates from alcohol in white needles, and melts at  $120-121^\circ$ ; silver acetate converts it into the diacetyl derivative of dibromosaligenin, and piperidine gives rise to dibromorthocresylpiperidine. The *acetyl* derivative of dibromosaligenin,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{OAc}$ , separates from alcohol in flattened, lustrous crystals, and melts at  $110-112^\circ$ ; the *diacetyl* derivative crystallises in needles, and melts at  $70-71^\circ$ .

M. O. F.

**Preparation of Cholesterol and Phytosterol from Animal and Plant Fats.** By A. JUCKENACK and ALBERT HILGER (*Arch. Pharm.*, 1898, 236, 367—369).—A reply to von Raumer (*Zeit. angew. Chem.*, 1898). The authors give the details of their method for the extraction of cholesterol and phytosterol from fats (compare *Forschungsber. Lebensmittel*, 1897, 119, 128, 151) and add that, in the place of sea-sand, which is often impure, they now employ small pieces of moistened filter paper free from fat; the extraction with ether is by this means rendered much easier and more complete. It is also preferable to saponify with caustic soda instead of caustic potash, because the hard soap thus formed is easier to dry and pulverise. The ether used for extracting the soap should be dried over metallic sodium.

A. W. C.

**Some Double Halogen Salts of Mercury.** By J. N. SWAN (*Amer. Chem. J.*, 1898, 20, 613—633).—*Aniline dimercurichloride*,  $\text{NH}_2\text{Ph} \cdot \text{HCl} \cdot 2\text{HgCl}_2$ , is best prepared by dissolving the theoretical quantities of aniline hydrochloride and mercuric chloride in boiling water acidified with hydrochloric acid; on cooling, beautiful, white crystals separate, which dissolve sparingly in cold water, but much more readily in methylic and ethylic alcohol. Although no aniline salt containing a larger proportion of mercuric chloride than this can be obtained, on dissolving molecular proportions of aniline hydrochloride and mercuric chloride in boiling water acidified with hydrochloric acid, crystals of *aniline mercurichloride*,  $\text{NH}_2\text{Ph} \cdot \text{HCl} \cdot \text{HgCl}_2$ , separate; the latter appears to be decomposed to some extent when allowed to crystallise slowly from ethylic or methylic alcohol. *Dianiline mercurichloride*,  $(\text{NH}_2\text{Ph})_2 \cdot 2\text{HCl} \cdot \text{HgCl}_2$ , prepared by adding an excess of aniline hydrochloride to a solution of mercuric chloride, crystallises in lustrous needles, and is much more soluble in water than either of the salts described above. No other compound of aniline with mercuric chloride could be obtained.

*Orthotoluidinemercurichlorides*.—(1),  $\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{HCl} \cdot 2\text{HgCl}_2$ , prepared from carefully purified orthotoluidine, separates from very dilute hydrochloric acid in beautiful, leaf-like crystals. (2),  $\text{C}_7\text{H}_7 \cdot \text{NH}_2 \cdot \text{HCl} \cdot \text{HgCl}_2$ , prepared by carefully heating a solution of mercuric chloride with a slight excess of toluidine hydrochloride to the boiling temperature, closely resembles the corresponding aniline derivative. (3),  $(\text{C}_7\text{H}_7 \cdot \text{NH}_2)_2 \cdot 2\text{HCl} \cdot \text{HgCl}_2$ , crystallises in lustrous needles or prisms, is easily soluble in water, and is decomposed by boiling alcohol.

*Metatoluidine mercurichlorides*.—(1),  $\text{C}_7\text{H}_7\text{NH}_2 \cdot \text{HCl} \cdot 2\text{HgCl}_2$ , crystal-

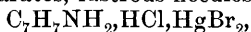


lises in thin plates, and is somewhat less soluble in water than the corresponding orthotoluidine and aniline salts, although closely resembling them. (2),  $C_7H_7 \cdot NH_2 \cdot HCl, HgCl_2$ , and

(3),  $(C_7H_7 \cdot NH_2)_2 \cdot 2HCl, HgCl_2$ , crystallise from very dilute hydrochloric acid in thin, lustrous plates.

*Paratoluidine mercurichloride*,  $C_7H_7 \cdot NH_2 \cdot HCl, HgCl_2$ , is much more soluble in hot than in cold water, and crystallises in beautiful, long needles; it is the only mercury double salt that can be obtained from paratoluidine.

The formation of mixed halogen double salts of mercury and the amines seems to be possible; on dissolving orthotoluidine hydrochloride (4 grams) and mercuric bromide (12 grams) in 75 c.c. of water acidified with hydrochloric acid, and removing the mercuric bromide which first separates, lustrous needles of the *salt*,



separate.

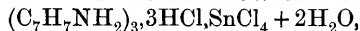
Although the salt,  $MgCl_2 \cdot 3HgCl_2 + 5H_2O$ , obtained by von Bonsdorff (*Ann. Phys. Chem.*, 1829, 17, 115) from magnesium and mercuric chloride was prepared by the author, the salt,  $MgCl_2 \cdot HgCl_2 \cdot 6H_2O$ , described as separating from the mother liquor could not be obtained. The mercury strontium salt to which von Bonsdorff gave the formula  $SrCl_2 \cdot 2HgCl_2 + 2H_2O$ , is regarded as having the formula,  $SrCl_2 \cdot 3HgCl_2 + xH_2O$ , analogous to that of the magnesium salt. The barium salt, described as  $BaCl_2 \cdot 2HgCl_2 + 2H_2O$ , appears rather to be  $BaCl_2 \cdot 3HgCl_2 + 8H_2O$ .  
W. A. D.

#### Double Halogen-salts of Tin with Aniline and the Toluidines.

By ROBERT L. SLAGLE (*Amer. Chem. J.*, 1898, 20, 633—646).—*Aniline stannochloride*,  $NH_2Ph \cdot HCl, SnCl_2 + H_2O$ , prepared by boiling a solution of molecular quantities of aniline hydrochloride and stannous chloride in very dilute hydrochloric acid, crystallises in orthorhombic tables,  $a:b:c = 0.4164:1:0.4608$ ; it is very soluble in hot water, sparingly in cold, and decomposes slowly in solution; in methylic and ethylic alcohol, it is extremely soluble. When heated, the salt commences to decompose at about  $70^\circ$ , and melts at about  $110^\circ$ ; on heating more strongly, stannous chloride sublimes. When a solution of aniline stannochloride in dilute hydrochloric acid is left for several hours, crystals of the anhydrous stannichloride,  $(NH_2Ph)_2 \cdot H_2SnCl_6$ , are deposited. *Dianiline stannochloride*,  $(NH_2Ph)_2 \cdot 2HCl, SnCl_2$ , prepared by adding stannous chloride (1 mol.) to a solution of aniline hydrochloride (2 mols.), separates in monosymmetric crystals, and is much more soluble in water than the monaniline salt. No other compounds of aniline with stannous chloride could be obtained.

*Dianiline stannichloride*,  $(NH_2Ph)_2 \cdot H_2SnCl_6 + 3H_2O$ , prepared by dissolving molecular quantities of stannic chloride and aniline hydrochloride in dilute hydrochloric acid and boiling, separates in sheaf-like aggregates of needles which rapidly effloresce. Anhydrous, transparent crystals, however, can also be obtained which are perfectly stable; these have been measured by Hiortdahl (*Zeit. Kryst. Min.*, 1882, 6, 484).

*Orthotoluidine stannochloride*,  $C_7H_7 \cdot NH_2, HCl, SnCl_2 + \frac{1}{2}H_2O$ , the only salt obtainable from orthotoluidine and stannous chloride, separates in white, opaque prisms. *Triorthotoluidine stannichloride*,



is formed on mixing solutions of orthotoluidine hydrochloride and stannic chloride in any proportion.

*Metatoluidine stannochloride*,  $C_7H_7NH_2, HCl, SnCl_2 + \frac{1}{2}H_2O$ , separates in silver-white, opaque crystals, and is the only stannous derivative obtainable from metatoluidine. *Dimetatoluidine stannichloride*,  $(C_7H_7NH_2)_2, H_2SnCl_6 + H_2O$ , crystallises in monosymmetric tables,  $a : b : c = 1.924 : 1 : 1.463$ ;  $\beta = 86^\circ 3'$ .

*Paratoluidine stannochloride*,  $C_7H_7NH_2, HCl, SnCl_2 + \frac{1}{2}H_2O$ , closely resembles the corresponding aniline derivative, and is much less soluble in water than *diparatoluidine stannichloride*,  $(C_7H_7NH_2)_2, H_2SnCl_6$ . *Diparatoluidine stannichloride* has been described by Hiortdahl (*loc. cit.*). W. A. D.

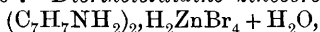
**Double Halogen-salts of Zinc with Aniline and the Toluidines.** By DANIEL BASE (*Amer. Chem. J.*, 1898, **20**, 646—663).—Dianiline zincochloride,  $(NH_2Ph)_2, H_2ZnCl_4 + H_2O$ , formed on mixing zinc chloride with aqueous aniline hydrochloride, has been described by Vohl (*Dingl. poly. J.*, 1865, 211); if an excess of the hydrochloride (3—6 mols.) is employed, *trianiline zincochloride*,  $(NH_2Ph)_3, 3HCl, ZnCl_2 + 2H_2O$ , separates in long, orthorhombic prisms; it is less soluble in alcohol and in water than the dianiline salt, and is stable in the air. It loses the whole of its contained water when dried over sulphuric acid, and can be heated to  $100^\circ$  without decomposing.

*Diorthotoluidine zincochloride*,  $(C_7H_7NH_2)_2, H_2ZnCl_4 + 2H_2O$  (Gräfinhoff, *J. pr. Chem.*, 1865, **95**, 221), is the only zinc double salt obtainable from orthotoluidine.

*Dimetatoluidine zincochloride*  $(C_7H_7NH_2)_2, H_2ZnCl_4$ , prepared by bringing together solutions of metatoluidine hydrochloride (1 mol.) and zinc chloride (2—3 mols.), separates from water, in which it is very soluble, in slender, silken needles. When a larger proportion of metatoluidine hydrochloride is employed, *trimetatoluidine zincochloride*,  $(C_7H_7NH_2)_3, 3HCl, ZnCl_2$ , is formed; it crystallises in slender needles, and is somewhat readily soluble in water.

*Diparatoluidine zincochloride*,  $(C_7H_7NH_2)_2, H_2ZnCl_4$ , formed on boiling a solution containing zinc chloride (1 mol.) and paratoluidine hydrochloride ( $\frac{1}{3}$ —3 mols.), crystallises in colourless plates, and dissolves easily in water. *Triparatoluidine zincochloride*,  $(C_7H_7NH_2)_3, 3HCl, ZnCl_2$ , formed in presence of an excess of paratoluidine hydrochloride, crystallises in well-defined, anorthic prisms.

*Dianiline zincobromide*,  $(NH_2Ph)_2, H_2ZnBr_4 + H_2O$ , the only double-salt obtainable from zinc bromide and aniline hydrobromide, separates in thick, colourless plates, is readily soluble in cold water, and does not decompose at  $110^\circ$ . *Diorthotoluidine zincobromide*,



forms large, colourless, prismatic plates which are readily soluble in cold water, and melt and decompose at about  $150^\circ$ . *Dimetatoluidine zincobromide*, with  $2H_2O$ , formed in a solution containing an excess of

zinc bromide, is with difficulty separated in a pure state from *trimetatoluidine zincobromide*,  $(C_7H_7NH_2)_3 \cdot 3HBr \cdot ZnBr_2$ , which generally accompanies it; the latter is, however, readily obtained pure from solutions containing an excess of metatoluidine hydrobromide, and crystallises in long, purple needles. *Diparatoluidine zincobromide* separates from solutions of paratoluidine hydrobromide containing an excess of zinc bromide, in thin, lustrous, colourless leaves; on attempting to crystallise it from water, paratoluidine hydrobromide separates.

By mixing solutions of zinc chloride and ammonium chloride in all proportions, only the two salts,  $ZnCl_2 \cdot 2NH_4Cl$  and  $ZnCl_2 \cdot 3NH_4Cl$ , described by Marignac (*Ann. des Mines*, 1857, [v], 12, 1) could be obtained.

Kane has stated (*Annalen*, 1849, 72, 290) that, on dissolving the compounds  $ZnCl_2 \cdot NH_3$  and  $ZnCl_2 \cdot 4NH_3$  in hydrochloric acid, corresponding double salts are formed; it appears, however, that the former gives rise to  $ZnCl_2 \cdot 2NH_4Cl$ , and the latter to  $ZnCl_2 \cdot 3NH_4Cl$ .

A complete bibliography of double chlorides, bromides, iodides, and fluorides of zinc with other metals and with organic bases is appended.

W. A. D.

**Schiff's Bases: Diphenamine Compounds of Aliphatic Aldehydes.** By ALEXANDER EIBNER (*Annalen*, 1898, 302, 335—370. Compare von Miller, Plochl and others, *Abstr.*, 1892, 1189).—Diphenamine compounds are Schiff's bases derived from an aldehyde and two molecular proportions of an amine; ethylenedianiline, a member of this class, has been recently described by the author (*Abstr.*, 1897, i, 464), and other bases of the same group have been investigated by Eberhardt and Welter (*Abstr.*, 1894, i, 451).

Contrary to the view of the last-named chemists, the presence of alkali is not necessary to the production of diphenamine compounds, which are best prepared by mixing cooled aqueous solutions of aldehyde and base; in cases where the substances are not soluble in water, solutions in dilute alcohol are employed.

*Ethyleneparanitrodiphenamine*,  $CHMe(NH \cdot C_6H_4 \cdot NO_2)_2$ , prepared from acetaldehyde and paranitraniline, crystallises in pale-yellow, attenuated needles, and melts at  $167^\circ$ ; repeated crystallisation from hot alcohol converts it into paranitraniline. The *nitrile*,  $C_9H_5N_3O_2$ , obtained by the action of hydrogen cyanide, crystallises from alcohol in golden-yellow needles, and melts at  $120^\circ$ .

*Ethyleneparachlorodiphenamine*,  $CHMe(NH \cdot C_6H_4Cl)_2$ , crystallises from a mixture of ether and alcohol in long, colourless needles or plates, and melts at  $64-65^\circ$ ; hydrogen cyanide converts it into the *nitrile*,  $C_6H_4Cl \cdot NH \cdot CHMe \cdot CN$ , which crystallises in leaflets melting at  $114.5^\circ$ , and is also produced when acetaldehyde is added to an ethereal solution of parachloraniline and hydrogen cyanide. The isomeric *nitrile*, obtained on adding chloroacetaldehyde to an ethereal solution of aniline and hydrogen cyanide, crystallises from alcohol in quadratic plates, and melts at  $83-84^\circ$ . An attempt to prepare chlorethylenediphenamine gave rise to a base, containing no halogen, melting at  $155^\circ$ .

*Chlorethylideneparachlorodiphenamine*,  $C_{14}H_{13}N_2Cl_3$ , obtained from choracetaldehyde and parachloraniline in ethereal solution, separates in beautiful, lustrous, rhombic crystals when light petroleum is added to the liquid; it melts at  $78-79^\circ$ . A base which melts at  $195^\circ$  is obtained when no medium is employed.

*Dichlorethylidenediphenamine*,  $C_{14}H_{14}N_2Cl_2$ , prepared from dichloroacetaldehyde and aniline without a diluent, crystallises in rhombic leaflets, and melts at  $70-71^\circ$ ; like the foregoing chloro-derivative, it is indifferent towards hydrogen cyanide.

*Trichlorethylidenediphenamine*,  $C_{14}H_{13}N_2Cl_3$ , has been described by Wallach; it is prepared from aniline and chloral hydrate, and melts at  $107.5^\circ$ . It is probable that the production of the additive compound,  $OH \cdot CHCl_3 \cdot NHPh$ , precedes the formation of this substance.

The *additive compound*,  $OH \cdot CHCl_3 \cdot NH \cdot C_6H_4Me$ , obtained from paratoluidine and chloral, crystallises in colourless, microscopic leaflets, and melts at  $75^\circ$ ; *trichlorethylideneparaditolamine*, described by Wallach, melts at  $115^\circ$ , and is obtained from the additive compound by exposure to air, by superfusion, and by treatment with hot water.

The *additive compound*,  $OH \cdot CHCl_3 \cdot NH \cdot C_6H_4 \cdot NO_2$ , prepared from paranitraniline and chloral, crystallises in aggregates and melts at  $128^\circ$ ; when the aldehyde is heated with the base in a reflux apparatus, *trichlorethylideneparanitrodiphenamine*,  $C_{14}H_{11}N_4O_4Cl_3$ , is produced and melts at  $218^\circ$ .

*Trichlorethylidenemetachlorodiphenamine*,  $C_{14}H_{11}N_2Cl_5$ , produced by the action of chloral on metachloraniline in ethereal solution, crystallises from alcohol in slender needles, and melts at  $89^\circ$ ; it is very stable, and undergoes no change when exposed to air or boiling water, being volatile in an atmosphere of steam.

*Trichlorethylideneparachlorodiphenamine*,  $C_{14}H_{11}N_2Cl_5$ , prepared from chloral and parachloraniline, crystallises from alcohol in short, lustrous prisms, and melts at  $143^\circ$ ; it is also very stable, and resists the action of boiling aqueous alkalis.

*Trichlorethylidenedichlorodiphenamine*,  $C_{14}H_9N_2Cl_7$ , is obtained by the action of chloral on 2:4-dichloraniline, and separates from ether in beautiful, lustrous crystals melting at  $144^\circ$ ; it is a remarkably stable substance, resisting the action of boiling alcoholic potash and of boiling acetic anhydride.

Chloral has no action on 1:2:4:6-trichloraniline or on symmetrical dichloronitraniline. M. O. F.

**Action of Nitrous Acid on Secondary Aromatic Amines.** By RICHARD STÖRMER (*Ber.*, 1898, 31, 2523—2541).—The question of the manner in which nitro-derivatives are produced by the action of nitrous acid on secondary aromatic amines is discussed at some length. It is found that if a nitrosamine having a nitro-group, or perhaps even a chlorine atom in the para-position, be treated with dilute nitric acid, a nitro-group enters the ring in the ortho-position. In the case of paranitrophenylnitrosamine, by the employment of the quantity of nitric acid theoretically necessary for the conversion of the nitroso- into a nitro-group, it may be almost entirely converted into dinitromethylaniline; the migration of the nitroso-group into

the ring, under the influence of alcoholic hydrochloric or sulphuric acid, was never observed; on the other hand, paranitromethylaniline does not yield any dinitro-compound under the foregoing conditions. The author concludes that the most plausible view of the sequence of changes is the following:  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NO} + \text{O} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NO}_2 = \text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NHMe}$ , the latter change being exactly similar to those observed by Bamberger (Abstr., 1893, i, 327, &c.) in the case of other nitramines.

1. [With PAUL HOFFMANN.]—A rapid stream of nitrous acid is passed into methylaniline suspended in water; after 2 hours, the paranitro-nitrosomethylaniline formed becomes crystalline, and may be separated by filtration; the substance may also be obtained by the action of nitric peroxide on methylaniline dissolved in cold ether. It is converted into paranitromethylaniline by hot hydrochloric acid, and when heated with dilute nitric acid (1 in 3) affords nearly the theoretical amount of 2:4-dinitromethylaniline; the latter was found to melt at  $176\text{--}177^\circ$  (corr.). If the quantity of nitric acid theoretically necessary be employed, the yield obtained is 88.2 per cent. of the possible amount.

*Acetoparanitromethylaniline*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMeAc}$ , produced by heating nitromethylaniline with acetic anhydride in closed tubes at  $175^\circ$  for 14 hours, melts at  $152\text{--}153^\circ$ . Gaseous nitrous acid causes replacement of the acetyl by the nitroso-group, and separation of the acetyl group is also effected by dilute nitric acid or alcoholic hydrogen chloride.

Paranitronitrosomethylaniline is not affected by warm hydrogen peroxide, alkaline ferricyanide, or by a solution of chromic anhydride in acetic acid; it is not altered after remaining in contact with a cold alcoholic solution of hydrogen chloride ( $1\frac{1}{2}$  per cent.) for 3 weeks.

2:4-Dinitronitrosomethylaniline,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{NMe} \cdot \text{NO}$ , made by passing a stream of nitrous acid into a cooled alcoholic solution of 2:4-dinitromethylaniline, closely resembles the corresponding mononitro-compound in regard to its stability towards different reagents; it crystallises from hot alcohol in flat, pale yellow needles, and melts at  $85\text{--}86^\circ$ .

*Paranitronitrosoethylaniline*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NEt} \cdot \text{NO}$ , crystallises from hot alcohol in straw-coloured needles and melts at  $119\text{--}120^\circ$ . When heated with dilute nitric acid, it yields 2:4-dinitroethylaniline; this was found to melt at  $113\text{--}114^\circ$ , and its nitroso-derivative,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_4$ , at  $51.5\text{--}52.5^\circ$ .

*Orthochloromethylaniline* is a pale-brown liquid boiling at  $215\text{--}216^\circ$  (corr.) under a pressure of 764 mm.; its sp. gr. = 1.1735 at  $11.5^\circ$ ; its nitroso-derivative is a liquid, and has a sp. gr. = 1.266 at  $15^\circ$ . Metachloromethylaniline was found to boil at  $234.5\text{--}235.5^\circ$  at 764 mm. pressure (compare La Coste and Bodewig, Abstr., 1885, 792), and has a sp. gr. = 1.174 at  $11.5^\circ$ ; its nitrosamine forms brown leaflets and melts at  $34\text{--}35^\circ$ .

*Metachlorethylaniline* is a brown liquid and boils at  $243\text{--}244^\circ$  at 760 mm. pressure; its sp. gr. = 1.120 at  $19^\circ$ ; its nitroso-compound is an oil having a sp. gr. = 1.227 at  $20^\circ$ . Parachloromethylaniline is oily, boils at  $239\text{--}240^\circ$  at 764 mm., and has a sp. gr. = 1.169 at  $11.5^\circ$ ;

the nitroso-derivative crystallises in prisms and melts at  $51^{\circ}$  (compare Koch, Abstr., 1887, 1041).

4-Chloromethylorthotoluidine, obtained from the corresponding chloronitrotoluene, is a colourless liquid which gradually assumes a greenish hue; it boils at  $248.5\text{--}249.5^{\circ}$  at 760 mm. pressure; its sp. gr. =  $1.138$  at  $19^{\circ}$ . The nitroso-derivative is an oil, and has a sp. gr. =  $1.226$  at  $20^{\circ}$ .

2:4-Chloronitronitrosomethylaniline,  $C_7H_6O_3N_3Cl$ , is obtained by acting on orthochloromethylaniline with nitrous acid; it forms yellowish-white needles and melts at  $94.5\text{--}95.5^{\circ}$ ; when boiled with strong hydrochloric acid, it yields pure 2:4-chloronitromethylaniline,  $C_7H_7O_2N_2Cl$ , which crystallises in small, sulphur-yellow needles and melts at  $116\text{--}117^{\circ}$ .

3-Chloronitronitrosomethylaniline,  $C_7H_6O_3N_3Cl$ , prepared by the long-continued action of nitrous acid on metachloromethylaniline, crystallises from hot alcohol in light-brown prisms and melts at  $67.5\text{--}68.5^{\circ}$ . 3-Chloronitromethylaniline,  $C_7H_7O_2N_2Cl$ , forms canary-yellow needles, and melts at  $106\text{--}107^{\circ}$ .

3-Chloronitronitrosoethylalaniline,  $C_8H_8O_3N_3Cl$ , crystallises in small, yellow needles and melts at  $75.5\text{--}76.5^{\circ}$ ; 3-Chloronitroethylalaniline,  $C_8H_9O_2N_2Cl$ , in yellow needles melting at  $75.5\text{--}76.5^{\circ}$ .

4:3(?) Chloronitronitrosomethylorthotoluidine,  $C_8H_8O_3N_3Cl$ , crystallises from alcohol in large, thick, pale yellow leaflets and melts at  $80.5\text{--}81.5^{\circ}$ . The corresponding chloronitromethyltoluidine,  $C_8H_9O_2N_2Cl$ , crystallises from alcohol in slender, bright yellow needles and melts at  $185\text{--}186^{\circ}$ ; on reduction with tin and hydrochloric acid, it yields a diamine which crystallises in brownish needles, melts at  $85^{\circ}$ , and when treated in hydrochloric acid solution with hydrogen sulphide and ferric chloride, affords a beautiful violet coloration, hence the base is probably a *paradiamine*.

4:2:6-Chlorodinitronitrosomethylaniline,  $C_7H_5O_5N_4Cl$ , is obtained in the usual manner from parachloromethylaniline, and is accompanied by 4:2-chloronitromethylaniline; it crystallises in flat, white needles, and melts at  $99\text{--}99.5^{\circ}$ . The corresponding chlorodinitromethylaniline,  $C_7H_6O_4N_3Cl$ , forms beautiful orange needles and melts at  $100\text{--}100.5^{\circ}$ .

3:5-Dinitronitrosomethylorthotoluidine crystallises in beautiful, shining, yellowish rhombohedra and melts at  $94\text{--}95^{\circ}$ . The corresponding dinitromethyltoluidine has already been obtained by Bamberger and Seitz (Abstr., 1897, i, 466).

Nitronitrosomethylmetatoluidine,  $C_8H_8O_3N_3$  [Me : N(NO)Me : NO<sub>2</sub> = 1:3:6(?)], forms elongated, yellowish leaflets and melts at  $73\text{--}74^{\circ}$ . The corresponding nitromethyltoluidine,  $C_8H_{10}O_2N_2$ , crystallises in yellowish-brown leaflets having a blue reflex, and melts at  $92\text{--}93^{\circ}$ .

Paranitronitrosodiphenylamine is readily obtained in quantitative amount by passing nitrous anhydride for 20 minutes through an ice cold solution of diphenylamine (5 grams) in alcohol (20—25 c.c.); it melts at  $133\text{--}134^{\circ}$ . If the action of the gas be prolonged (3 hours), an orange, crystalline mass, sparingly soluble in alcohol and melting at  $156\text{--}170^{\circ}$ , is formed (compare Meldola, Ber., 1878, 11, 351). The nitronitroso-compound is also readily obtained by adding a few drops of nitric peroxide to a solution of nitrosodiphenylamine in dry carbon

bisulphide. If a solution in chloroform is used, separation of symmetrical *paradinitrodiphenylamine*,  $\text{NH}(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , occurs after 2 hours; this substance crystallises from hot alcohol in yellow needles having a blue shimmer, and melts at  $214\text{--}214.5^\circ$ . Under certain conditions, *orthoparadinitrodiphenylamine* (m. p. =  $156.5\text{--}157^\circ$ ) is formed in small quantity, and also a *trinitrodiphenylamine*,  $\text{C}_{12}\text{H}_8\text{N}_4\text{O}_6$ , melting at  $170\text{--}173^\circ$ . *Paranitronitrosodiphenylamine* yields *paradinitrodiphenylamine* by the action of dilute nitric acid.

[With KURT DRAGENDORFF.]—When nitrous acid acts on tetrahydroquinoline dissolved in water or alcohol, a product is obtained which, when roughly purified, melts at  $137\text{--}138^\circ$  (compare Hoffmann and Königs, Abstr., 1883, 1143), but which in reality consists of two substances, one crystallising in beautiful, shining needles and melting at  $154\text{--}155^\circ$ , and the other forming red-brown needles and melting at  $99\text{--}100^\circ$ ; the former is probably *4-nitro-1'-nitrosotetrahydroquinoline*,  $\text{NO}_2\cdot\text{C}_9\text{H}_9\cdot\text{NO}$ , and the latter the corresponding *2-nitro*-compound. Both yield the respective nitrotetrahydroquinolines on treatment with hydrochloric acid, but the para-derivative does not give a dinitro-compound on treatment with dilute nitric acid.

*4-Nitrotetrahydroquinoline*,  $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$ , forms dark yellow needles having a bluish metallic sheen, and melts at  $163\text{--}164^\circ$ . *2-Nitrotetrahydroquinoline*,  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$ , crystallises in shining, red needles and melts at  $82\text{--}83^\circ$ . Both of these are feeble bases, dissolving in acids, and being reprecipitated on addition of water.

*1-Nitro-1'-nitroso-3-methyltetrahydroquinoline*,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$ , produced by the action of nitrous anhydride on tetrahydroquinoline, forms beautiful, yellow needles and melts at  $122^\circ$ . It is accompanied by two other substances. The first of these is the corresponding *1-nitrotetrahydro-3-methylquinoline*,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ ; it forms beautiful, dark red, rectangular tables and melts at  $103\text{--}105^\circ$ ; it is also obtained by hydrolysis of the nitronitroso-compound with boiling alcohol. The second substance is probably a *2 (or 4)-nitro-3-methyltetrahydroquinoline*,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ ; it crystallises in long, yellowish, feathery needles, melts at  $67^\circ$ , and is a stronger base than its isomeride.

*3-Nitro-1-nitroso-1-methyltetrahydroquinoline*,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$ , forms small, bright-yellow needles, melts at  $100\text{--}102^\circ$ , and dissolves sparingly in alcohol, but readily in a mixture of alcohol and benzene. The corresponding *3-nitro-1-methyltetrahydroquinoline*,  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2$ , forms dark-yellow crystals having a bluish, metallic sheen and melts at  $142^\circ$ ; it dissolves readily in alcohol.

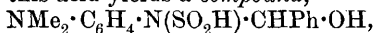
When nitrous anhydride is led into an alcoholic solution of tetrahydroquinaldine, Müller's nitronitrosotetrahydroquinaldine (m. p. =  $152\text{--}153^\circ$ ) is formed, and is accompanied by a small quantity of *1(?)-nitronitrosotetrahydroquinaldine*,  $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3$ , which melts at  $105\text{--}107^\circ$ . *3-Nitrotetrahydroquinaldine*,  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ , forms dark, brownish-red crystals having a metallic lustre, and melts at  $130\text{--}132^\circ$ .

Two isomeric nitronitroso-derivatives,  $\text{C}_9\text{H}_9\text{O}_3\text{N}_3$ , may be obtained from hydromethylketole. One, probably the *1-nitro*-compound, forms dark yellow crystals and melts at  $108^\circ$ ; the second, doubtless the *paranitro*-derivative, separates in yellow crystals and melts at  $135^\circ$ .

3-Nitrohydroketole,  $C_9H_{10}O_2N_2$ , forms brown needles with a beautiful, metallic lustre and melts at  $82^\circ$ .

3-Nitro-1'-nitrosohydro-2'-phenylindole,  $C_{14}H_{11}O_3N_3$ , is obtained in bright yellow, shining crystals and melts at  $160^\circ$ . It was not accompanied by any isomeric, and did not yield any crystalline product on hydrolysis. A. L.

**Thionyl Compounds of Substituted Paraphenylenediamines.** By A. FRANCKE (*Ber.*, 1898, 31, 2179—2182. Compare Abstr., 1893, i, 518; and 1898, i, 431).—Thionylparamidodimethylaniline,  $NMe_2 \cdot C_6H_4 \cdot N : SO$ , is obtained by treating amidodimethylaniline with thionyl chloride in benzene solution; it is dark red with a greenish surface lustre, and melts at  $72^\circ$ . In the air, it becomes converted gradually into the yellow thionamic acid,  $NMe_2 \cdot C_6H_4 \cdot NH \cdot SO_2H$ , which is more readily obtained by passing sulphurous anhydride into an ethereal solution of amidodimethylaniline. With benzaldehyde in alcoholic solution, this acid yields a compound,



which is white, melts at  $150^\circ$ , and when heated, or treated with alkalis, forms parabenzyldeneamidodimethylaniline,  $NMe_2 \cdot C_6H_4 \cdot N : CHPh$ . When thionylamidodimethylaniline is heated with dimethylaniline and zinc chloride in a sealed tube at  $100^\circ$ , some methylene-blue is formed, but only in very small amount.

Thionylparamidodiethylaniline,  $NEt_2 \cdot C_6H_4 \cdot N : SO$ , melts at  $36^\circ$ ; the hydrochloride melts at  $170^\circ$ , and is decomposed by water; the thionamic acid melts at  $122$ — $124^\circ$ .

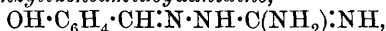
Paramidomethylbenzylaniline, prepared by reducing nitrosomethylbenzylaniline, boils at  $290$ — $295^\circ$ ; thionylparamidomethylbenzylaniline,  $CH_2Ph \cdot NMe \cdot C_6H_4 \cdot N : SO$ , melts at  $94^\circ$ .

Thionylamidodiphenylamine,  $NHPh \cdot C_6H_4 \cdot N : SO$ , melts at  $142^\circ$ , and is fairly stable.

Thionyl-1-amidodinaphthylamine,  $C_{10}H_7 \cdot NH \cdot C_{10}H_6 \cdot N : SO$ , melts at  $120^\circ$ , and is the most stable of all these compounds. C. F. B.

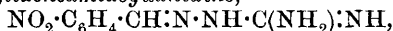
**Condensation of Amidoguanidine with Aromatic Aldehydes and Ketones.** By JOHANNES THIELE and RICHARD BIHAN (*Annalen*, 1898, 302, 299—311. Compare Abstr., 1892, 1297).—Aqueous solutions of an amidoguanidine salt are agitated with an aldehyde or its alcoholic solution, when one drop of a mineral acid induces condensation.

Orthohydroxybenzylideneamidoguanidine,



crystallises from chloroform in lustrous leaflets and melts at  $102^\circ$ ; the nitrate and hydrochloride crystallise in long needles, and melt at  $209$ — $210^\circ$  and  $215$ — $216^\circ$  respectively. Protracted treatment with boiling alkali converts the substance into orthohydroxybenzylideneazine, obtained by Curtius and Pflug from hydrazine and salicylaldehyde. Parahydroxybenzylideneamidoguanidine crystallises from water in plates containing  $1H_2O$  and melts at  $204^\circ$ ; the nitrate melts and decomposes at  $216^\circ$ .

Orthonitrobenzylideneamidoguanidine,

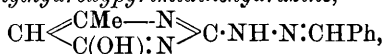




crystallises in long, orange-yellow needles and melts at  $185^{\circ}$ ; the *nitrate* melts and decomposes at  $251^{\circ}$ . *Metanitrobenzylideneamidoguanidine* crystallises in yellow, highly refractive needles, which melt and decompose at  $210^{\circ}$ ; the *nitrate* melts at  $247^{\circ}$ . *Paranitrobenzylideneamidoguanidine* has been described by Wedekind (Abstr., 1897, i, 241); the *nitrate* melts and decomposes at  $241^{\circ}$ . The paranitro-compound contains  $1\text{H}_2\text{O}$ , and melts at  $198^{\circ}$  (Wedekind gives  $206^{\circ}$ ); it is produced along with the ortho-derivative when benzylideneamidoguanidine nitrate is added to concentrated sulphuric acid.

The *diacetyl* derivative of benzylideneamidoguanidine crystallises from water, and melts at  $158\text{--}159^{\circ}$ .

*Benzylidenemethylhydroxypyrimidinehydrazine*,

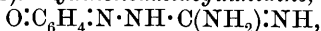


prepared from benzylideneamidoguanidine and ethylic acetoacetate, crystallises from alcohol; it contains  $1\text{H}_2\text{O}$ , and melts at  $232\text{--}233^{\circ}$ . Boiling hydrochloric acid eliminates benzaldehyde, and gives rise to hydrazine and methyluracil, described by Behrend.

*Diphenylamidotriazine*,  $\text{N} \begin{array}{c} \diagup \text{CPh} \text{---} \text{CPh} \\ \diagdown \text{N:C(NH}_2\text{)} \end{array} \text{N}$ , obtained from amidoguanidine nitrate and benzil, crystallises from alcohol, and melts at  $175^{\circ}$ ; the *acetyl* derivative melts at  $151^{\circ}$ .

*Amidophenantriazine*,  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C:N} \cdot \text{N} \\ \text{C}_6\text{H}_4 \cdot \text{C:N} \cdot \text{CNH}_2 \end{array}$ , prepared from amidoguanidine and phenanthrenequinone, crystallises from alcohol in pale yellow needles and melts at  $262^{\circ}$ .  
M. O. F.

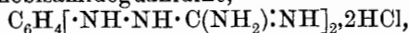
**Condensation of Amidoguanidine and of Semicarbazide with Quinones.** By JOHANNES THIELE and WILLY BARLOW (*Annalen*, 1898, 302, 311—332).—*Quinoneamidoguanidine*,



forms slender, cherry-red needles, soluble in hot water, but dissolving sparingly in alcohol and ether; it begins to decompose at  $208^{\circ}$ , and melts at  $212\text{--}215^{\circ}$ . Excess of boiling caustic potash eliminates ammonia and gives rise to phenol. The *nitrate*, prepared by heating amidoguanidine nitrate (1 mol.) with alcoholic quinone in a reflux apparatus, crystallises from water in slender, orange-yellow needles; it melts and decomposes at about  $186^{\circ}$ . The *hydrochloride* forms red crystals melting at about  $173^{\circ}$ , and the *picrate* crystallises in yellow needles, and melts with previous decomposition at  $232^{\circ}$ ; the *potassium* derivative crystallises in golden-yellow leaflets, and becomes red and absorbs moisture when exposed to air. The *hydrochloride* of dihydroquinoneamidoguanidine,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{C(NH}_2\text{):NH}$ , HCl, forms colourless crystals and melts at  $208^{\circ}$ .

*Quinonebisamidoguanidine*,  $\text{C}_6\text{H}_4[\text{:N} \cdot \text{NH} \cdot \text{C(NH}_2\text{):NH}]_2$ , crystallises in cherry-red needles and melts at  $250^{\circ}$ , decomposing somewhat below this temperature; boiling aqueous potash eliminates ammonia, and gives rise to a small proportion of phenylhydrazine. The *nitrate*, obtained from amidoguanidine nitrate (2 mols.) and quinone, crystallises in yellow needles, and does not melt below  $280^{\circ}$ ; the *hydrochloride* forms needles, and also remains unfused at  $280^{\circ}$ . The *hydrochloride*

of dihydroquinonebisamidoguanidine,

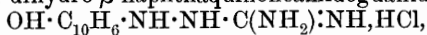


forms colourless crystals and melts at  $223^\circ$ .

*α-Naphthaquinoneamidoguanidine*,  $\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$ , dissolves with great difficulty in water, but is more freely soluble in alcohol; it decomposes at  $222^\circ$ , and melts at about  $233^\circ$ . The *nitrate* forms slender, yellow needles, and melts at about  $253^\circ$ , whilst the *hydrochloride* decomposes at about  $235^\circ$ ; the *sulphate* decomposes at  $260^\circ$ , and the *picrate* melts indefinitely at about  $272^\circ$ .

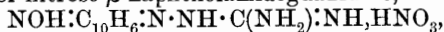
*α-Naphthaquinonebisamidoguanidine*,  $\text{C}_{10}\text{H}_6[\cdot\text{N}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}]_2$ , crystallises in orange-yellow needles, and decomposes when its solutions are evaporated; on heating the substance with alkalis, naphthalene is produced, and naphthylhydrazine is not among the products. The *nitrate*, forming yellowish-green needles, does not melt below  $277^\circ$ ; and the *sulphate*, which crystallises from water in yellow needles containing  $1\text{H}_2\text{O}$ , melts at  $260^\circ$ , previously undergoing decomposition.

*β-Naphthaquinoneamidoguanidine* decomposes and sublimes at  $175\text{--}180^\circ$ , and melts at about  $202^\circ$ ; the *nitrate* and *hydrochloride* crystallise in orange yellow needles, and decompose at  $217^\circ$  and  $278^\circ$  respectively. When the base is heated with aqueous potash, *α*-naphthol and the compound  $\text{C}_{11}\text{H}_7\text{N}_3\text{O}$  are formed; the latter crystallises from its solution in alcohol, which has a red colour and exhibits green fluorescence, and yields *sodium* and *silver* derivatives. The *hydrochloride* of dihydro-*β*-naphthaquinoneamidoguanidine,



forms colourless needles containing  $1\text{H}_2\text{O}$ .

The *nitrate* of nitroso-*β*-naphtholamidoguanidine,



melts at about  $145^\circ$ , and yields no precipitate with ammonia. The compound,  $\text{C}_{11}\text{H}_8\text{N}_4\text{O}$ , obtained by the elimination of the elements of ammonium nitrate through the agency of boiling water, separates from alcohol in yellow crystals, and melts above  $240^\circ$ ; the *hydrochloride* forms compact, red crystals, and the *nitrate* is decomposed by water. Reduction with stannous chloride and hydrochloric acid renders the substance colourless, yielding the crystalline *hydrochloride*,  $\text{C}_{11}\text{H}_{10}\text{N}_4\cdot\text{HCl}$ , which melts and decomposes at  $225^\circ$ ; ferric chloride liberates from this salt the compound,  $\text{C}_{11}\text{H}_8\text{N}_4$ , which crystallises from alcohol in needles melting at  $201^\circ$ , and forms a *hydrochloride* and *nitrate*.

*Quinonesemicarbazone*,  $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , prepared from alcoholic quinone and semicarbazide hydrochloride (1 mol.), crystallises from petroleum in small, yellow needles, and melts at  $172^\circ$ ; it dissolves readily in alkalis, which, on boiling, give rise to phenol. *Quinonedisemicarbazone*,  $\text{C}_6\text{H}_4(\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$ , forms a fine, red, crystalline powder, and melts at about  $243^\circ$ ; boiling alkalis produce phenylhydrazine.

*α-Naphthaquinonesemicarbazone*,  $\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , separates from glacial acetic acid in greenish-yellow crystals melting at  $247^\circ$  after undergoing decomposition; alkalis give rise to *α*-naphthol. *β-Naphthaquinonesemicarbazone* crystallises from alcohol in golden-yellow leaflets, and decomposes at  $184^\circ$ .

*Quinoneoximesemicarbazone*,  $\text{NOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}$ , crystallises

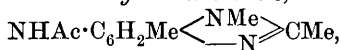
in slender, brownish-yellow needles when the solution in glacial acetic acid is poured into much water; it decomposes at about 238°.

*Nitroso-β-naphtholsemicarbazone*,  $\text{NOH}:\text{C}_{10}\text{H}_6:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , forms yellow needles and melts at about 189°. M. O. F.

**History of Phenylhydroxylamine.** By ALFRED WOHL (*Ber.*, 1898, 31, 2543).—The author repeats his claim to priority (*Abstr.*, 1894, i, 409) in the discovery of phenylhydroxylamine. A. L.

**Regularities of Substitution in the Formation of Azo-colouring Matters.** By JOHANNES PINNOW and A. MATCOVITCH (*Ber.*, 1898, 31, 2514—2523. Compare *Abstr.*, 1896, i, 161 and 427).—*Diamidodimethylparatoluidine*,  $\text{C}_9\text{H}_{15}\text{N}_3$ , is obtained by reducing the product of interaction of orthamidodimethylparatoluidine and diazobenzenesulphonic acid with stannous chloride and hydrochloric acid; it boils at 193.5° (uncorr.) under 40 mm. pressure, and melts, after sintering slightly, at 60—61°. The *picrate*,  $\text{C}_9\text{H}_{15}\text{N}_3\cdot 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms brilliant, rhombohedral, yellowish-brown tables, melts at 157—158°, dissolves readily in acetone and hot water, less readily in cold alcohol, ethylic acetate, and chloroform, and only sparingly in ether or benzene; it is insoluble in light petroleum. The *hydrobromide* crystallises in tables, and dissolves very readily in water and alcohol. The *diacetyl* derivative,  $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_2$ , forms rhombic tables and melts at 235—236°.

2-Acetamido-3:1':2'-trimethylbenzimidazole,



produced when diamidodimethylparatoluidine is heated with acetic anhydride under pressure at 154—158°, crystallises from water or alcohol in prisms, or slender, shining needles, and melts at 237—238°. As the production of this substance from amidodimethyltoluidine is attended with the loss of a methyl group, it follows that an amido-group in the parent substance is in the ortho-position relatively to the dimethylamido-group. The *picrate*,  $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms small, sulphur-yellow needles, melts at 264°, dissolves readily in hot acetic acid, ethylic acetate, and alcohol, but only sparingly in the cold solvents and in acetone. 2-Amido-3:1':2'-trimethylbenzimidazole,  $\text{C}_{10}\text{H}_{13}\text{N}_3$ , prepared from the acetyl derivative by hydrolysis with hot hydrochloric acid, crystallises in slender needles, melts at 237—237.5°, and dissolves in most organic media, with the exception of ether and light petroleum. The *hydrochloride*,  $\text{C}_{10}\text{H}_{13}\text{N}_3\cdot 2\text{HCl}$ , crystallises from hydrochloric acid in anhydrous needles, and does not melt below 295°. The *picrate*,  $\text{C}_{10}\text{H}_{13}\text{N}_3\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms a dense, bright yellow, crystalline powder and melts and effervesces at 265°; it is somewhat readily soluble in hot acetic acid, but is sparingly soluble in the cold liquid and in the usual organic solvents. 3:1':2'-Trimethylbenzimidazole-2-azo-β-naphthylamine,  $\text{C}_{20}\text{H}_{19}\text{N}_5$ , crystallises from alcohol in slender, yellowish-red prisms and melts and decomposes at 254—257°; it dissolves readily in acetic acid and hot ethylic acetate, but is only sparingly soluble in acetone and ether.

*Metadinitrodimethylparatoluidine*,  $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_4$ , obtained from dinitroparatoluidine by the action of a large excess of dilute nitric and

sulphuric acids at 15—17°, crystallises from light petroleum in thick, red needles, melts at 95°, and dissolves readily in the usual organic media, with the exception of cold alcohol and light petroleum. Its constitution follows from the fact that it yields metadinitrotolyl-methylnitramine under the influence of fuming nitric acid. *Acetamidodinitrodimethylparatoluidine*,  $C_{11}H_{15}N_3O_3$ , is made from the foregoing compound by reduction with alcoholic ammonium sulphide, followed by treatment with acetic anhydride; it crystallises from light petroleum in bright yellow needles and melts at 97°.

*Metadiamidodimethylparatoluidine*,  $C_9H_{15}N_3$ , obtained by reducing dinitrodimethyltoluidine with tin and hydrochloric acid, crystallises from light petroleum in long, white, striated needles, melts at 54·5—56·5°, and boils at 189° under 22 mm. pressure. The *hydrochloride*,  $C_9H_{15}N_3 \cdot 2HCl$ , crystallises from hydrochloric acid in needles or prisms, melts at 221—225°, and is less readily soluble in water and hydrochloric acid than its isomeride. The *picrate*,  $C_9H_{15}N_3 \cdot 2C_6H_3N_3O_7$ , forms thick, sulphur-yellow needles, and melts at 142—143°. The *diacetyl* derivative,  $C_{13}H_{10}N_3O_2$ , crystallises from ethylic acetate in bundles of long needles, and melts at 151—152°.

1-*Acetamido-3 : 1' : 2'-trimethylbenzimidazole*, produced on heating diamidodimethylparatoluidine with acetic anhydride in sealed tubes, crystallises in long, slender needles from methylic alcohol, and in this state has the composition  $2C_{12}H_{15}N_3O + MeOH$ ; it melts at 199—201°. The *picrate*,  $C_{12}H_{15}N_3O \cdot C_6H_3N_3O_7$ , separates from glacial acetic acid in bundles of sulphur-yellow needles and melts at 158—159·5°. 1-*Amido-3 : 1' : 2'-trimethylbenzimidazole*,  $C_{10}H_{13}N_3$ , crystallises from methylic alcohol in needles which have the composition  $2C_{10}H_{13}N_3 + MeOH$ ; it melts at 129—130°, dissolves readily in hot acetone and methylic alcohol, and moderately readily in the cold liquids and hot water. The *hydrochloride*,  $C_{10}H_{13}N_3 \cdot 2HCl$ , crystallises in rectangular plates and does not melt below 285°. The *picrate*,  $C_{10}H_{13}N_3 \cdot C_6H_3N_3O_7$ , melts at 224—225°. 3 : 1' : 2'-*Trimethylbenzimidazole-1-azo-β-naphthylamine*,  $C_{20}H_{19}N_5$ , forms red prisms having a green surface colour and melts at 258—259°.

The compound,  $C_{15}H_{18}N_4SO_3$ , obtained when metamidodimethylparatoluidine is treated with diazobenzenesulphonic acid, forms a readily dissociated acetate which crystallises from alcohol in cube-like forms and melts at 205—206°; on hydrolysis, it yields diamidodimethylparatoluidine which boils at 198—202° and forms a diacetyl derivative; the latter crystallises from methylic alcohol in rhombic tables and melts at 234·5—236°. These compounds and the corresponding acetamidotrimethylbenzimidazole are identical with those obtained in a similar manner from orthamidodimethylparatoluidine; it follows that when diazobenzenesulphonic acid acts on metamidodimethylparatoluidine, it is the hydrogen in the meta-position with regard to the dimethylamido-group which is replaced, hence the dimethylated amido-group exercises no directive influence on the substitution. A. L.

**Formation of Phenylhydrazides by the action of Phenylhydrazine on Organic Acids in the Cold.** By VIRGIL L. LEIGHTON (*Amer. Chem. J.*, 1898, 20, 676—679).—On dissolving

phenylhydrazine in a slight excess of cold formic acid, and allowing the solution to stand during 24 hours, 71·7 per cent. of the theoretical amount of formophenylhydrazide is obtained. Cold acetic and propionic acids act more slowly on phenylhydrazine, 61 per cent. of the theoretical amount of  $\beta$ -acetophenylhydrazide being produced during 4 days in the former, and 86·6 per cent. of propionophenylhydrazide during 5 days in the latter case.

A 25 per cent. yield only of *isobutyrophenylhydrazide*,  $N_2H_2Ph \cdot COPr^\beta$ , was obtained from cold isobutyric acid and phenylhydrazine after 7 days; the hydrazide is nearly insoluble in water, and crystallises from alcohol in rectangular or hexagonal plates and melts at 142—143°.

Forty-seven per cent. of the theoretical amount of *isohexophenylhydrazide*,  $N_2H_2Ph \cdot CO \cdot C_6H_{11}$ , is formed from cold isohexoic acid during 5 days; it separates from light petroleum in thin, transparent crystals and melts at 144—145°.

From heptioic acid, 86·4 per cent. of the *heptophenylhydrazide*,  $N_2H_2Ph \cdot CO \cdot C_6H_{13}$ , required by theory is formed during 6 days, the latter crystallises from alcohol in thin, transparent prisms and melts at 103—104°.

In acetic acid, as in aqueous solution, 1-phenyl-5-pyrazolone-3-carboxylic acid is formed by the action of phenylhydrazine on acetylenedicarboxylic acid; in presence of an excess of the hydrazine, however, a totally different crystalline substance is obtained, which is being investigated by the author.

W. A. D.

**Orthohydroxyguanazyl Benzene.** By EDGAR WEDEKIND (*Ber.*, 1898, 31, 2353—2354. Compare *Abstr.*, 1898, i, 453).—The free base *orthohydroxybenzylideneamidoguanidine*, obtained by saturating an alkaline solution of amidoguanidine nitrate and salicylaldehyde with carbonic anhydride, forms colourless needles, melts at 100—102°, and dissolves easily in warm water, alcohol, chloroform, and benzene, and sparingly in ether and petroleum.

*Orthohydroxyguanazylbenzene*,



produced by adding a solution of diazobenzene chloride, neutralised with caustic soda, to a dilute alcoholic solution of the above base, crystallises from alcohol in light yellow prisms, and melts at 191—192°, is soluble in the usual organic solvents, and develops an intense yellowish-red coloration with solutions of the alkalis.

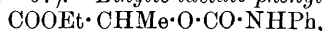
G. T. M.

**Action of Cyanamide on Chloranil in presence of Potassium Hydroxide.** By H. IMBERT (*Compt. rend.*, 1898, 126, 1879—1882).—When 4 molecular proportions of potassium hydroxide are added to a boiling aqueous solution of cyanamide (2 mols.) containing finely-powdered chloranil (1 mol.) in suspension, the compound  $CN_2 \cdot C_6Cl_2(OK)_2 : CN_2 + 2H_2O$  is obtained, and crystallises from water in brownish-green needles with a metallic lustre. It becomes anhydrous at 105°. The silver salt is brown, insoluble, and anhydrous.

When the potassium salt is boiled with excess of potassium

hydroxide, ammonia is liberated, and potassium carbonate and potassium chloranilate are formed. It follows that the product of the action of potassium hydroxide and cyanamide on chloranil differs from chloranilic acid in containing two  $\text{CN}_2$ -groups in place of the quinonic oxygen atoms. The hydrogen compound,  $\text{CN}_2 \cdot \text{C}_6\text{Cl}_2(\text{OH})_2 \cdot \text{CN}_2$ , seems to form bluish-black crystals, but has not yet been isolated in a pure state. Under certain conditions, the action of concentrated hydrochloric acid on the potassium compound yields a precipitate and liberates a gas; the precipitate seems to be a mixture of the compound  $\text{CN}_2 \cdot \text{C}_6\text{Cl}_2(\text{OH})_2 \cdot \text{O}$  with a condensed product of the nature of an acetal (compare Abstr., 1898, i, 411). C. H. B.

**Phenylurethanes derived from the Ethereal Salts and Nitriles of some Hydroxy-acids.** By EUGÈNE LAMBLING (*Compt. rend.*, 1898, 127, 64—67).—*Ethyllic lactate phenylurethane*,



obtained by heating at  $180^\circ$  a mixture of ethylic lactate with phenylcarbimide in molecular proportion, is a brown oil which cannot be crystallised, and decomposes, when distilled under diminished pressure, with formation of diphenylcarbamide. When treated with 10 per cent. soda in the cold, it is converted into *sodium lactate phenylurethane*, which crystallises from alcohol in microscopic prisms, and this, with dilute hydrochloric acid, yields the corresponding *acid*, which crystallises in microscopic tablets melting at  $139$ — $140^\circ$ ; this is slightly soluble in water, readily soluble in sodium carbonate solution, alcohol, and ether, and less soluble in chloroform, from which it crystallises in fine needles. *Ethyllic trichlorolactate phenylurethane*,  $\text{COOEt} \cdot \text{CH}(\text{CCl}_3) \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , from ethylic trichlorolactate and phenylcarbimide, crystallises from a mixture of ether with light petroleum in needles melting at  $57.5^\circ$ ; it is slightly soluble in water, and soluble in organic solvents. On treatment with soda, it yields an internal anhydride which will be described hereafter. *Trichlorolactonitrile phenylurethane*,  $\text{CCl}_3 \cdot \text{CH}(\text{CN}) \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , obtained by heating a mixture of chloral cyanhydrate with phenylcarbimide at  $130$ — $140^\circ$ , crystallises in hexagonal tablets melting at  $115$ — $116^\circ$  and is soluble in organic solvents. *Ethyllic glycollate phenylurethane*,  $\text{COOEt} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , the preparation of which is similar to that of the preceding compounds, crystallises in microscopic prisms melting at  $65^\circ$ ; it is fairly soluble in boiling water, more so in alcohol and ether. When boiled with soda, a solution is obtained from which hydrochloric acid precipitates *glycollic acid phenylurethane* in quadrangular tablets melting at  $134$ — $135^\circ$ , and soluble in alcohol and ether. *Glycollonitrile phenylurethane*,  $\text{CN} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from a mixture of ether with light petroleum in stellate groups of microscopic prisms melting at  $74$ — $75^\circ$ . *Ethyllic phenylglycollate phenylurethane*,  $\text{COOEt} \cdot \text{CHPh} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises in cauliflower-like masses of microscopic needles melting at  $93^\circ$ , and soluble in alcohol, ether, and chloroform. When treated with the theoretical quantity of soda, it at first dissolves, and then gives a crystalline precipitate of phenylglycolanilide,  $\text{OH} \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NHPh}$ , a substance already obtained by Haller; the mother liquor, on

adding hydrochloric acid, yields *phenylglycollic acid phenylurethane*, which crystallises in microscopic needles. *Phenylglycollonitrile phenylurethane*,  $\text{CN} \cdot \text{CHPh} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from a mixture of ether with light petroleum in microscopic prisms melting at  $105^\circ$ . *Ethyllic  $\beta$ -hydroxybutyrate phenylurethane*,  $\text{COOEt} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , was obtained as a reddish-brown oil, insoluble in water but soluble in alcohol and ether, which could not be distilled or crystallised. *Ethyllic  $\alpha$ -hydroxyisobutyrate phenylurethane*,  $\text{COOEt} \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from a mixture of light petroleum with a little ether, in long, silky needles melting at  $77.5^\circ$ , soluble in chloroform, very soluble in alcohol and ether. When boiled for a short time with the theoretical quantity of soda, a solution is obtained which, on cooling, deposits glistening scales of  *$\alpha$ -hydroxyisobutyranilide*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{NHPh}$ , a compound already prepared by Tigerstedt. The mother liquor from these crystals, when acidified with hydrochloric acid, yields microscopic needles of  *$\alpha$ -hydroxyisobutyric acid phenylurethane*, which melt at  $130^\circ$ , and are soluble in alcohol and ether, less so in chloroform.

It appears, from the formation of the compounds described, that the groups CN, Ph, CO, and  $\text{CCl}_3$  exercise no perceptible influence on the interaction of the neighbouring hydroxyl with phenylcarbimide, and it would also seem that the latter acts as readily on tertiary as on primary and secondary hydroxyl groups. This is confirmed by its action on tertiary butylic and tertiary amylic alcohols. The phenylurethanes, which were produced in nearly the theoretical amount, crystallised respectively in silky needles melting at  $134$ – $135^\circ$ , and in microscopic prisms melting at  $42^\circ$ .  
N. L.

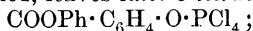
**Orthophenylthiohydantoic Acid.** By RIZZO NICCOLÒ (*Gazzetta*, 1898, 28, ii, 68–71).—In continuation of his work on Jäger's phenylthiohydantoic acid (*Abstr.*, 1898, i, 659), the author has examined the orthophenylthiohydantoic acid which P. Mayer obtained by the interaction of phenylthiocarbamide with ammonium chloracetate, and finds that it has the constitution,  $\text{NHPh} \cdot \text{C}(\text{NH})\text{S} \cdot \text{CH}_2 \cdot \text{COOH}$ , assigned to it by Mayer.

When treated with potash and benzoic chloride, the acid yields benzoylphenylcyanamide, whilst potash alone converts the acid into phenylcyanamide. Orthophenylthiohydantoic acid is soluble in caustic alkalis, but not in alkali carbonates; it may therefore possibly be an internal salt of the constitution

$$\begin{array}{c} \text{C}(\text{NH}) \cdot \text{S} \cdot \text{CH}_2 \\ | \qquad \qquad | \\ \text{NH}_2\text{Ph} \cdot \text{O} \cdot \text{CO} \end{array}$$

W. J. P.

**Salol-O-phosphinic Acid.** By AUGUST MICHAELIS and W. KERKHOFF (*Ber.*, 1898, 31, 2172–2179).—Salol (1 mol.) reacts vigorously with phosphoric chloride ( $1\frac{1}{3}$  mols.), and the product, after being purified by treatment with sulphurous anhydride and warming under diminished pressure to expel the thionyl chloride and phosphorus oxychloride that is formed, leaves *salol-O-tetrachlorophosphine*,



this melts at  $44^\circ$ , and is unusually stable in the presence of water. A bye-product in the reaction, when the latter is too violent, is *phenylic orthochlorobenzoate*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{COOPh}$ , which may be obtained readily,

together with phosphorus oxychloride, by heating the phosphine at  $180\text{--}200^\circ$ ; it melts at  $37^\circ$ . When the phosphine is treated for several hours with sulphurous anhydride at  $130\text{--}135^\circ$ , thionyl chloride and *salol-O-oxychlorophosphine*,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{POCl}_2$ , are formed; the latter melts at  $70\text{--}71^\circ$ , and boils, decomposing slightly, at  $125\text{--}135^\circ$  under 13 mm. pressure. When the tetrachlorophosphine is dissolved in benzene and treated with a little water, *salol-O-phosphinic acid*,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{OH})_2 + \text{H}_2\text{O}$  (the water is lost over sulphuric acid or at  $58\text{--}60^\circ$ ), is formed; this melts at  $62^\circ$ , or when anhydrous at  $88^\circ$ . It is decomposed by hot alkalis into phenol, salicylic acid, and phosphoric acid; by cold alkalis, into phenol and *salicyl-O-phosphinic acid*; by hot water, or not too dilute acids, into salol and phosphoric acid. The *silver* salt,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{P}(\text{OAg})_4$ , and *lead* salt,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}\cdot\text{O}_2\text{Pb}$ , were prepared and analysed, as also the *aniline* salt,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{OH})\cdot\text{ONH}_3\text{Ph}$ , and the analogous *phenylhydrazine* salt, which melt at  $161^\circ$  and  $141^\circ$  respectively. *Diethylsalol-O-phosphinate*,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{OEt})_2$ , prepared by heating the tetrachlorophosphine with sodium ethoxide suspended in benzene, boils at  $105\text{--}115^\circ$  under 13 mm. pressure; the *diphenylic* salt, prepared in an analogous manner, melts at  $76\text{--}77^\circ$ . By treating the tetrachlorophosphine with aniline, *salol-O-phosphinic dianilide*,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{NHPh})_2$ , melting at  $174\text{--}175^\circ$ , is formed; the *diparatoluidide* and *diphenylhydrazide*, prepared in a similar manner, melt at  $146^\circ$  and  $170^\circ$  respectively. An *oxyphosphazo-compound*,  $\text{COOPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{PO}\cdot\text{NPh}$  (probably double this), was obtained by heating the oxychlorophosphine with aniline hydrochloride and a little xylene for 12 hours at  $180^\circ$ ; it melts at  $152^\circ$ . C. F. B.

#### Direct Introduction of Mercury into Aromatic Compounds.

By OTTO DIMROTH (*Ber.*, 1898, 31, 2154—2156. Compare K. A. Hofmann, *Abstr.*, 1898, i, 635).—When benzene is heated for several hours with dry mercuric acetate at  $110^\circ$ , phenylmercuric acetate,  $\text{Ph}\cdot\text{Hg}\cdot\text{OAc}$ , is formed. Toluene gives an analogous derivative. Phenol and mercuric acetate react in concentrated aqueous solution, when the liquid is warmed; *hydroxyphenyldimercuric acetate*,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{Hg}\cdot\text{OAc})_2$ , melting at  $216\text{--}217^\circ$ , separates out, whilst on treating the mother liquor with sodium chloride, *para-* and *ortho-hydroxyphenylmercuric chlorides*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ , melting respectively at  $219\text{--}220^\circ$  and  $152\cdot5^\circ$ , can be obtained; these form sodium derivatives, and by boiling the sodium derivatives with methylic iodide and alcohol, *para-* and *ortho-anisylmercuric chlorides* can, in the last two cases, be obtained. All these compounds are decomposed by hydrochloric acid, the mercury being removed and hydrogen substituted for it; in the case of the phenolic compounds, iodine also removes the mercury and forms iodophenols. C. F. B.

**Derivatives of Anisaldehyde.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 510—515).—Claisen has shown that ethylic acetate reacts with benzaldehyde in the presence of sodium, yielding, as chief product, ethylic cinnamate (*Abstr.*, 1890, 891). The author has obtained *ethylic paramethoxycinnamate* by a similar method, the best yield being obtained at a temperature of  $15^\circ$ ; as the reaction is



exothermic, the mixture is surrounded by iced water, and after it has been allowed to remain for 12 hours, acetic acid and water are added. The ethylic salt distils between  $295^{\circ}$  and  $320^{\circ}$ , and crystallises in brilliant plates melting at  $49^{\circ}$ . The yield is good if the materials employed are pure; the ethylic acetate should contain neither alcohol nor water. *Paramethoxycinnamic acid* crystallises from dilute alcohol in long, silky needles melting at  $170^{\circ}$  (compare Abstr., 1887, 1109). The *dibromide*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{COOEt}$ , melts at  $114^{\circ}$ . *Paramethoxyphenylpropionic acid*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{C}\cdot\text{COOH}$ , obtained when the dibromide is subjected to prolonged treatment with excess of alcoholic potash, is sparingly soluble in water, softens at  $132^{\circ}$ , and melts and decomposes at  $139^{\circ}$ . The yield is about 40 per cent. of the theoretical. *Paramethoxyphenylacetylene*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{CH}$ , formed when the preceding acid is heated with excess of aniline until the evolution of carbonic anhydride ceases, boils at  $205\text{--}212^{\circ}$ , forms fairly large crystals melting at  $28\cdot5^{\circ}$ , and is insoluble in water, but dissolves in alcohol or ether, and yields precipitates with ammoniacal cuprous chloride or silver nitrate. The yield is poor.

*Anisyl methyl ketone*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , formed when paramethoxyphenylpropionic acid is heated with water at  $130^{\circ}$ , may be purified by distillation in steam and treatment with light petroleum, when crystals consisting of large plates, and melting at  $38\cdot5^{\circ}$ , are obtained. A further quantity of the ketone, together with methoxyphenylacetylene, may be separated from the petroleum solution.

*Ethylic methylenedioxcinnamate*,  $\text{CH}_2\langle\text{O}\rangle\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{COOEt}$ , obtained when ethylic acetate is treated with piperonal in the presence of metallic sodium, melts at  $65\text{--}68^{\circ}$ . J. J. S.

**Action of Chloracetic Chloride on various Aromatic Hydrocarbons in the presence of Aluminium Chloride.** By A. COLLET (*Bull. Soc. Chim.*, 1897, [iii], 17, 506—510).—Chloracetylbenzene (*o*-chloracetophenone),  $\text{CH}_2\text{Cl}\cdot\text{COPh}$ , is readily obtained by Friedel-Craft's method, either at the ordinary temperature or at the boiling point of benzene. When heated again with more benzene and aluminium chloride, it remains unaltered, but when treated with toluene (150 grams to 10 of chloracetophenone) and aluminium chloride (20 grams) at the boiling point of the toluene, it yields *methyldeoxybenzoin*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , which may be purified by distillation under diminished pressure and subsequent recrystallisation from boiling alcohol; it crystallises in small, colourless needles melting at  $84\text{--}85^{\circ}$ .

Chloracetic chloride (50 grams), toluene (200 grams), and aluminium chloride ( $65\text{--}70$  grams) react at the ordinary temperature, yielding *parachloracetyltoleune* (*p*-tolyl chloromethyl ketone),  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , [ $\text{Me}:\text{CO}=1:4$ ], which distils at  $260\text{--}263^{\circ}$  and melts at  $55\cdot5\text{--}56^{\circ}$ . When oxidised, it yields terephthalic acid. When heated with an alcoholic solution of potassium acetate, it yields colourless needles of *paratoluoylcarbinol acetate*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$ , melting at  $83\text{--}83\cdot5^{\circ}$ . Aniline and parachloracetyltoleune, in alcoholic solution, yield *paratolyl anilidomethyl ketone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHPh}$ , which crystallises

in yellow plates melting at 118—120°. When parachloroacetyltoiuene is heated with an excess of toluene and aluminium chloride, it yields *deoxytoluoin* (tolyl methylbenzyl ketone),  $C_6H_4Me \cdot CO \cdot CH_2 \cdot C_6H_4Me$ , which crystallises in colourless needles melting at 97—98°. A small quantity of the same substance is obtained when chloroacetic chloride is boiled with toluene. *Chloroacetylparaxylylene* (paraxylyl chloromethyl ketone),  $C_6H_3Me_2 \cdot CO \cdot CH_2Cl$  [1:4:2], is obtained when a mixture of paraxylylene (25 grams) and chloroacetic chloride (27 grams) is added slowly to aluminium chloride (25 grams) covered with a layer of carbon bisulphide; when recrystallised from alcohol or benzene, it melts at 31—32°, and when oxidised with alkaline permanganate it yields trimellitic acid.

*Chloroacetylmesitylene* (*mesityl chloromethyl ketone*),  $C_6H_2Me_3 \cdot CO \cdot CH_2Cl$ , obtained in a similar manner, melts at 68.5°, and is sparingly soluble in alcohol; the yield is good.

*Chloroacetyldiphenyl*,  $C_6H_4Ph \cdot CO \cdot CH_2Cl$ , is obtained by dissolving diphenyl (10 grams) in an excess of carbon bisulphide, adding aluminium chloride (10 grams) and then gradually chloroacetic chloride (8 grams); it crystallises from boiling alcohol and melts at 122—123°. When oxidised, it yields paradiphenylcarboxylic acid. J. J. S.

**Coumarin.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 515—517).—Salicylaldehyde has been acetylated by Barbier's method (*Compt. rend.*, 90, 37). The acetyl derivative,  $COH \cdot C_6H_4 \cdot OAc$ , is readily obtained when the aldehyde (1 mol.) is heated with acetic anhydride (2 mols.) for 6 hours at 180°, but if an excess of the anhydride is employed, namely, double the weight of the aldehyde, coumarin is formed, agreeing in all its properties with coumarin obtained by other methods. J. J. S.

**Action of Organic Acids on Nitriles.** By JOHN A. MATHEWS (*J. Amer. Chem. Soc.*, 1898, 20, 648—668).—When malonic acid is heated with succinonitrile in a sealed tube during  $5\frac{1}{2}$  hours at 150°, considerable decomposition occurs, and a small quantity of succinimide is formed, but no malonimide; when malononitrile is heated with glacial acetic acid, it is almost completely decomposed. On heating cyanacetic acid dissolved in benzene at 190°, it is largely decomposed, although a small quantity of a crystalline *substance* is formed, which melts at 115°, contains nitrogen, and is easily soluble in alcohol, ether, and acetone, but insoluble in benzene; it appears to consist of *malonimide*, since it is converted into malonic acid when boiled with aqueous potash.

On heating benzoic acid (1 mol.) with succinonitrile (1 mol.), initially during 7 hours at 145°, and subsequently for  $5\frac{1}{2}$  hours at 195°, benzonitrile is formed, together with succinimide; when an excess of benzoic acid (2 mols.) is employed, the same products are formed, a considerable proportion of the acid remaining unacted on. Since no succinic acid was obtained, the author considers that the production of succinimide probably takes place through the intermediate formation of  $\beta$ -cyanopropionic acid, the latter undergoing rearrangement at the temperature employed.

When a mixture of phenylacetic acid and succinonitrile, in molecular proportion, is heated at  $150^{\circ}$  during 6 hours, phenylacetoneitrile is formed, together with a small quantity of phenylacetamide; the latter is probably formed by a small quantity of water present interacting with phenylacetoneitrile. When an excess of phenylacetic acid is used (2 mols. to 1 of nitrile), it is not completely acted on under the above conditions; phenylacetoneitrile is obtained together with diphenyldiacetamide, the latter being formed by the interaction of benzylic cyanide with the excess of phenylacetic acid.

On heating salicylic acid with acetonitrile during 5 hours at  $195-200^{\circ}$ , considerable decomposition occurs and small quantities of phenol are formed, although no other product can be isolated.

Anthranilic acid is decomposed when heated with acetonitrile for 5 hours at  $220-230^{\circ}$ , a product almost completely soluble in water being obtained; the aqueous solution deposits slender *crystals* which melt at  $232^{\circ}$  and readily sublime, and are converted by boiling concentrated hydrochloric acid into a crystalline *substance* which does not melt at  $280^{\circ}$ . On heating phthalic acid with propionitrile during  $5\frac{1}{2}$  hours at  $180-200^{\circ}$ , a 92.5 per cent. yield of phthalimide is obtained; the action, however, seems to be complete in  $3\frac{1}{2}$  hours. A mixture of phthalic acid and succinonitrile, in molecular proportion, is considerably charred when heated during 5 hours at  $220^{\circ}$ , phthalimide being formed, together with small quantities of succinimide. Phthalic anhydride does not interact with acetonitrile when heated initially during 4 hours at  $145^{\circ}$ , and, finally, for  $13\frac{1}{2}$  hours at  $200-235^{\circ}$ ; its behaviour, therefore, does not resemble that of acetic anhydride, which easily gives rise to triacetamide under the same conditions. Terephthalic acid is not changed when heated with propionitrile at  $260^{\circ}$ . On heating homophthalic acid with acetonitrile during 5 hours at  $190^{\circ}$ , only a small quantity of homophthalimide is obtained, a non-nitrogenous crystalline *substance*, which decomposes and chars at  $230^{\circ}$  being formed, together with white *crystals* which melt at no definite temperature. Cyanorthotoluic acid, when heated in benzene solution at  $190^{\circ}$ , is not converted into homophthalimide (compare Gabriel, *Ber.*, 1887, 20, 2502), but a small quantity of a *substance*, which crystallises in needles and melts at  $182^{\circ}$ , is formed.

When diphenic acid is heated with acetonitrile during 6 hours at  $225-240^{\circ}$ , acetic acid is formed, together with a 90 per cent. yield of diphenimide; the latter melts at  $217.5^{\circ}$ , whilst diphenamide melts at  $212-213^{\circ}$  when slowly heated, and at  $217^{\circ}$  when heated rapidly (compare Graebe and Aubin, *Abstr.*, 1889, 145; and Wegerhoff, *Abstr.*, 1888, 1200).

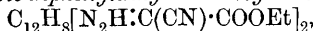
It is usually stated that orthosulphobenzoic acid melts at  $250^{\circ}$ , whereas it really melts at  $68^{\circ}$  when containing water of crystallisation, and at  $130^{\circ}$  when anhydrous; the ammonium hydrogen salt,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{NH}_4$ , which was originally considered to be the free acid, melts at  $250-260^{\circ}$ . When orthosulphobenzoic acid (1 mol.) is heated with acetonitrile (1 mol.) for 5 hours at  $165-170^{\circ}$ , benzoic sulphinide (saccharin) is not formed, but a small quantity of a *substance* isomeric with it, having no sweet taste; the latter separates

from alcohol in minute crystals, and is possibly the *unsymmetrical sulphobenzimide*,  $\text{SO}_2 < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{C:NH}$ .

On heating mellitic acid (1 mol.) with acetonitrile (3 mols.) containing a few drops of acetic anhydride during 4 hours at  $265-275^\circ$ , somewhat impure paramide is obtained; when the mixture is heated initially at  $180-200^\circ$  for 3 hours, subsequently at  $225-235^\circ$ , during the same period, a 90 per cent. yield of paramide is obtained, together with a small quantity of euchroic acid. An attempt to prepare mellitomonimide by heating acetonitrile (1 mol.) with mellitic acid (1 mol.) during  $4\frac{1}{2}$  hours at  $215-220^\circ$ , gave rise to a large quantity of euchroic acid only; a similar attempt, using tetrasodium mellitate, failed, no action taking place at  $290^\circ$ . Anhydrous euchroic acid is not changed by heating with acetonitrile during  $3\frac{1}{2}$  hours at  $223^\circ$ , but at  $240-260^\circ$  it is partially converted into paramide; this reaction indicates that euchroic acid is an ortho-compound. A *para-euchroic acid*,  $\text{C}_{13}\text{H}_4\text{N}_2\text{O}_8 + 2\text{H}_2\text{O}$ , appears to be formed when disodium mellitate (1 mol.) is heated with acetonitrile (2 mols.) during 5 hours at  $225-240^\circ$ ; it crystallises from water in thin plates, and does not melt or change, except by losing water of crystallisation, when heated at  $295^\circ$ . It resembles euchroic acid in giving the euchrone test, but differs from it in not yielding paramide when heated with propionitrile during 5 hours at  $240-260^\circ$ . In making the euchrone test for euchroic acid (compare Schwartz, *Annalen*, 1848, 66, 46), aluminium amalgam can be used instead of zinc; the action takes place slowly, the aluminium becoming red before the solution shows any colour.

In all the experiments described above, a few drops of acetic anhydride were present to insure anhydrous conditions. W. A. D.

**Action of Aromatic Tetrazochlorides on Methylic and Ethylic Cyanacetates.** By G. FAVREL (*Compt. rend.*, 1898, 127, 116—117. Compare Abstr., 1893, i, 210, 465, 509; 1895, i, 274, and 1896, i, 479).—*Ethylic diphenyldihydrazonocyanacetate*,



produced by adding an alcoholic solution of ethylic cyanacetate to a cold solution of diphenyltetrazochloride and subsequently rendering the mixture alkaline, is a yellow powder melting at  $204-206^\circ$ , and insoluble in the usual organic solvents, but crystallising from aniline; with alcoholic soda, it yields a disodium derivative. The corresponding *dimethylic* salt melts and decomposes at  $270^\circ$ .

*Ethylic diorthotolyldihydrazonocyanacetate* is obtained from diazotised tolidine and ethylic cyanacetate, and melts at  $224-225^\circ$ . The *methylic* salt melts at  $270^\circ$ .

*Ethylic dianisyldihydrazonocyanacetate* melts at  $283-285^\circ$ .

G. T. M.

**Action of Tetramethyldiamidobenzhydrol on Para- and Meta-sulphanilic Acids.** By SUAIS (*Bull. Soc. Chim.*, 1897, [iii], 17, 517—519).—Tetramethyldiamidobenzhydrol (54 grams) is dissolved in a solution of sodium parasulphanilate (46·2 grams) and

hydrochloric acid (18 c.c.), in 1 litre of water. The whole is heated at 80—90° during 6 hours, and the products are (1) a yellow, crystalline product which dyes cotton, mordanted with tannic acid, in much the same way as auramines, and is very sensitive to acids. (2) A sulpho-leuco-base which is transformed by lead peroxide into a dye which colours wool green, and is sensitive to alkalis, which decolorise it. (3) Hexamethyltriimidotriphenylmethane. (4) A substance remaining in solution which has not been examined.

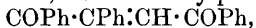
A mixture of 34 grams of metasulphanilic acid, 51 grams of the benzhydrol, 530 c.c. of water, and 57 c.c. of hydrochloric acid, when heated on the water bath for from 6 to 12 hours, gives the same products as above, but the yellow substance only forms some 4 per cent. of the total products, the sulpho-leuco-base being the chief constituent. The last compound can be converted into green and blue colouring matters.

J. J. S.

**Formation of Carbocyclic Compounds from 1:5- and 1:6-Diketones by Converting them into their Pinacones.** By JOHANNES WISLIGENUS (*Annalen*, 1898, 302, 191—195. Compare Pusch, Abstr., 1895, i, 666).—The paper introduces the following, which deal with the formation of cyclic compounds on reducing certain diketones.

M. O. F.

**Dibenzoyldiphenylbutadiene and its Reduction to Tetraphenylbenzene.** By JOHANNES WISLIGENUS and ADOLF LEHMANN (*Annalen*, 1898, 302, 195—214. Compare Japp and Miller, Trans., 1885, 11).—According as benzil condenses with one or two molecular proportions of acetophenone, 1:2-dibenzoylphenylethylene,



or dibenzoyldiphenylbutadiene,  $\text{C}_2\text{Ph}_2(\text{CH} \cdot \text{COPh})_2$ , is produced; the former has been already described by Japp and Miller under the name dehydroacetophenonebenzil.

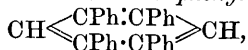
*Dibenzoyldiphenylbutadiene*,  $\text{C}_2\text{Ph}_2(\text{CH} \cdot \text{COPh})_2$ , crystallises in yellow needles and melts at 191—192°; the *dioxime* melts and decomposes at 246°. Bromine converts the diketone into a *dibromide* which decomposes at about 170°, and into a tetrabromide. Reduction with zinc dust and glacial acetic acid converts the diketone into a variety of compounds, the separation of which is described in detail in the original paper; the following are the substances in question.

*Dibenzoyldiphenylbutane*,  $\text{C}_2\text{H}_2\text{Ph}_2(\text{CH}_2 \cdot \text{COPh})_2$ , melts at 243—247°.

*Dibenzoyldiphenylbutene*,  $\text{COPh} \cdot \text{CH} : \text{CPh} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{COPh}$ , melts at 220—222°; the *dioxime* crystallises in six-sided plates, and melts at 230°.

*Tetraphenyldihydroxydihydrobenzene*,  $\text{CH} \begin{array}{c} \text{CPh}(\text{OH}) \cdot \text{CPh}(\text{OH}) \\ \text{CPh} \text{---} \text{CPh} \end{array} \text{CH}$ ,

crystallises from boiling alcohol in colourless, monoclinic prisms, and melts at 170—171°; the *pinacoline*,  $\text{C}_{30}\text{H}_{22}\text{O}$ , obtained from it by elimination of  $1\text{H}_2\text{O}$ , crystallises from boiling alcohol in thin, yellow needles, and melts at 180—181°. *Tetraphenylbenzene*,



separates from boiling benzene in colourless needles, and melts at 277—278°; Bogdanowska has described an isomeric hydrocarbon which melts at 268—269° (Abstr., 1892, 851).

M. O. F.

**Ethyl 1:2-Dibenzoylglutarate and its Conversion into 1:2-Diphenylcyclopentane.** By JOHANNES WISLICENUS and CRISTOPH KARL KUHN (*Annalen*, 1898, 215—222).—*Ethyl 1:2-dibenzoylglutarate*,  $\text{CH}_2(\text{CHBz}\cdot\text{COOEt})_2$ , may be prepared by the action of methylenic iodide on ethyl benzoylacetate under the influence of sodium ethoxide (compare Knoevenagel, *Abstr.*, 1895, i, 48); it crystallises from ether in small, lustrous needles, and melts at  $130.5^\circ$ . An alcoholic solution is indifferent towards ferric chloride, but the latter develops a cherry red coloration with the oily modification of the ethereal salt which is associated with the crystals.

**1:3-Dibenzoylpropane**,  $\text{CH}_2(\text{CH}_2\text{Bz})_2$ , obtained along with  $\gamma$ -benzoylbutyric acid by hydrolysing the oil with 10 per cent. caustic potash, crystallises in nacreous needles and melts at  $67.5^\circ$ ; the *dioxime* forms elongated, lustrous prisms and melts at  $62^\circ$ .

The *pinacone*,  $\text{C}_{17}\text{H}_{18}\text{O}_2$ , prepared by reducing dibenzoylpropane, is a yellow oil, which, with hydriodic acid and red phosphorus at  $150\text{--}160^\circ$ , yields **1:2-diphenylcyclopentane**,  $\begin{array}{c} \text{CHPh}\cdot\text{CH}_2 \\ | \\ \text{CHPh}\cdot\text{CH}_2 \end{array} > \text{CH}_2$ , crystallising from a mixture of ether and alcohol and melting at  $108^\circ$ .

M. O. F.

**1:3-Dibenzoyl-1:3-diphenylpropane and its Reduction to Tetraphenylcyclopentane.** By JOHANNES WISLICENUS and HAROLD CARPENTER (*Annalen*, 1898, 302, 223—236).—**1:3-Dibenzoyl-1:3-diphenylpropane**,  $\text{CH}_2(\text{CHPh}\cdot\text{COPh})_2$ , prepared by the action of formaldehyde on deoxybenzoin under the influence of caustic potash, melts at  $145.5\text{--}146.5^\circ$ ; it is structurally isomeric with deoxybenzoinbenzylideneacetophenone which melts at  $189^\circ$  (*Abstr.*, 1895, i, 48).

**1:2:3:5-Tetraphenylcyclopentane-1:2-diol**,  $\begin{array}{c} \text{OH}\cdot\text{CPh}\cdot\text{CHPh} \\ | \\ \text{OH}\cdot\text{CPh}\cdot\text{CHPh} \end{array} > \text{CH}_2$ ,

the pinacone obtained by reducing dibenzoyldiphenylpropane, occurs in two forms, according as an acidic or alkaline reducing agent is employed. When prepared by means of zinc dust and glacial acetic acid, it crystallises from alcohol in needles and melts at  $138^\circ$ ; the modification obtained through the agency of sodium amalgam, however, crystallises in colourless, lustrous needles and melts at  $239\text{--}240^\circ$ .

**Tetraphenylcyclopentane**,  $\begin{array}{c} \text{CHPh}\cdot\text{CHPh} \\ | \\ \text{CHPh}\cdot\text{CHPh} \end{array} > \text{CH}_2$ , prepared by reducing the pinacones with hydriodic acid and red phosphorus at  $140\text{--}150^\circ$ , crystallises from alcohol in colourless lustrous needles, and melts at  $80.5\text{--}81^\circ$ .

**Tetraphenylcyclopentadiene**,  $\begin{array}{c} \text{CPh}\cdot\text{CPh} \\ | \\ \text{CPh}\cdot\text{CPh} \end{array} > \text{CH}_2$ , arises from the action of oxalic acid at  $138^\circ$  on the pinacone first described; it crystallises from a mixture of alcohol and benzene, and melts at  $177^\circ$ . The *dibromide*,  $\text{C}_{29}\text{H}_{20}\text{Br}_2$ , crystallises from alcohol in small, red plates and melts at  $151.5\text{--}152^\circ$ .

**2:3:5:6-Tetraphenylpyridine**,  $\text{CH} \begin{array}{c} \text{CPh}\cdot\text{CPh} \\ \text{CPh}\cdot\text{CPh} \end{array} \text{N}$ , is prepared by heating 1:3-dibenzoyl-1:3-diphenylpropane with alcoholic hydroxyl-

amine hydrochloride at  $150^{\circ}$ ; it melts at  $233.5^{\circ}$ , that is to say,  $54.5^{\circ}$  higher than 2:4:5:6-tetraphenylpyridine (Knoevenagel, *loc. cit.*).

M. O. F.

**Derivatives of Benzylidenediacetophenone: 1:2:4-triphenylcyclopentane.** By JOHANNES WISLIGENUS and FRANK H. NEWMAN (*Annalen*, 1898, 302, 236—244).—1:2:4-Triphenylcyclopentane-1:2-diol,  $\begin{array}{c} \text{OH} \cdot \text{CPh} \cdot \text{CH}_2 \\ \text{OH} \cdot \text{CPh} \cdot \text{CH}_2 \end{array} > \text{CHPh}$ , is the pinacone prepared by

reducing benzylidenediacetophenone (Abstr., 1896, i, 556) with zinc dust and acetic acid; it crystallises from light petroleum and melts at  $142^{\circ}$ .

1:2:4-Triphenylcyclopentadiene,  $\begin{array}{c} \text{CPh} \cdot \text{CH} \\ \text{CPh} \cdot \text{CH} \end{array} > \text{CHPh}$ , formed by the action of concentrated hydrochloric acid on the pinacone dissolved in alcohol, crystallises in yellowish needles and melts at  $149^{\circ}$ . The dibromide,  $\text{C}_{23}\text{H}_{16}\text{Br}_2$ , melts at  $157^{\circ}$ .

1:2:4-Triphenylcyclopentane,  $\begin{array}{c} \text{CHPh} \cdot \text{CH}_2 \\ \text{CHPh} \cdot \text{CH}_2 \end{array} > \text{CHPh}$ , prepared by heating the unsaturated hydrocarbon with hydriodic acid at  $160$ — $170^{\circ}$ , is a pale yellow oil, and boils at  $285^{\circ}$  under a pressure of 50 mm.

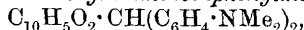
1:3:6-Triphenylpyridine,  $\text{CPh} \begin{array}{c} \text{CH} \cdot \text{CPh} \\ \text{CH} \cdot \text{CPh} \end{array} \text{N}$ , produced by the action of hydroxylamine hydrochloride in a reflux apparatus, crystallises from alcohol in colourless prisms, and melts at  $137.5^{\circ}$ . Free hydroxylamine, on the other hand, converts benzylidenediacetophenone into the *oxime* and the *dioxime* which melt at  $144^{\circ}$  and  $163.5^{\circ}$  respectively.

M. O. F.

**New Reaction for Paraquinones and Paraquinoidal Compounds.** By RICHARD MÖHLAU (*Ber.*, 1898, 31, 2351—2352).—Benzhydrol and its derivatives combine with paraquinones and similarly constituted compounds, the condensation being accompanied by elimination of water. Benzoquinone and benzhydrol give rise to benzoquinonebidiphenylmethane,  $\text{C}_6\text{H}_2\text{O}_2(\text{CHPh}_2)_2$ , which crystallises in yellow prisms and melts at  $238^{\circ}$ .

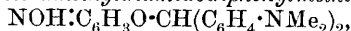
If one of the hydrogen atoms adjacent to a quinone oxygen atom is already substituted, then only one hydrol residue enters the quinone molecule. In this manner,  $\alpha$ -naphthaquinonediphenylmethane,  $\text{C}_{10}\text{H}_5\text{O}_2 \cdot \text{CHPh}_2$ , results from the action of benzhydrol on  $\alpha$ -naphthaquinone; it crystallises in yellow prisms and melts at  $185^{\circ}$ .

$\alpha$ -Naphthaquinonetetramethyldiamidodiphenylmethane,



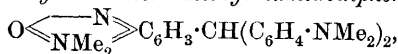
is produced from  $\alpha$ -naphthaquinone and tetramethyldiamidodiphenylcarbinol; it forms dark red leaflets melting at  $167^{\circ}$ .

Paranitrosophenoltetramethyldiamidodiphenylmethane,



produced from tetramethyldiamidodiphenylcarbinol and paranitrosophenol, forms dark yellow prisms and melts at  $217^{\circ}$ .

Paranitrosodimethylanilinetetramethyldiamidodiphenylmethane,



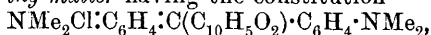
the analogous compound from nitrosodimethylaniline, crystallises in yellow prisms and melts at  $212^{\circ}$ .

Paraquinonoid dyes form similar condensation products.

A blue colouring matter obtained from Meldola's blue and the above diamidohydrol is described in the D.R.-P. No. 68381.

These condensation products behave as leuco-bases of the triphenylmethane series, and on oxidation yield colouring matters which contain two chromophoric groups.

A blue colouring matter having the constitution



is obtained by oxidising  $\alpha$ -naphthaquinonetetramethyldiamidodiphenylmethane with lead peroxide.

G. T. M.

**Constitution of the Dinitro-derivative obtained by the Nitration of  $\beta$ -Naphthol.** By FRIEDRICH KEHRMANN and M. MATIS (*Ber.*, 1898, 31, 2418—2419).—The nitro-compound obtained by the nitration of  $\beta$ -naphthol can also be prepared from dinitro- $\beta$ -naphthylamine. The last compound can readily be converted into a dinitro-naphthalene, which, on reduction, yields a diamido-derivative, and this is converted by Sandmeyer's reaction into 1:3'-dichloronaphthalene. The *diamido*-compound is, therefore, 1:3'-diamidonaphthalene, and the original dinitro- $\beta$ -naphthylamine has the constitution  $[(\text{NO}_2)_2:\text{NH}_2 = 1:3':2]$ , since it is already known that the two groups in the same ring are in the ortho-position (Loewe, *Abstr.*, 1891, 1424). Hence dinitro- $\beta$ -naphthol has the constitution  $[\text{OH}:(\text{NO}_2)_2 = 2:1:3']$ .

A. H.

**Naphthopicric Acid.** By FRIEDRICH KEHRMANN and WANDA HABERKANT (*Ber.*, 1898, 31, 2420—2424).—The commercial product prepared by the nitration of "Martius' yellow" contains, in addition to naphthopicric acid, a trinitronaphthol which melts at  $145^{\circ}$ , and is converted by oxidation into 1:2:4-nitrophthalic acid, and therefore has the constitution  $[\text{OH}:(\text{NO}_2)_3 = 1:2:4:2' \text{ or } 3']$ , the exact position of one nitro-group not having been as yet ascertained. Naphthopicric acid is converted by reduction into diamidonaphthaquinonimide, as previously described by Diehl and Merz (*Abstr.*, 1878, 250). When this substance is boiled with water, it is converted into a mixture of 1'-amido-2-hydroxy-1:4-naphthaquinone and 2:1'-diamido-1:4-naphthaquinone. The former of these crystallises in dark brown plates melting at  $221^{\circ}$ , and forms a blood-red solution in alkalis, whilst the *diacetyl* derivative crystallises in orange-yellow granules; 2:1'-diamido-1:4-naphthaquinone, on the other hand, is insoluble in alkalis, and crystallises in dark red tablets which decompose above  $200^{\circ}$ . No hydroxynaphthaquinonimide derivative could be obtained. The trinitronaphthol melting at  $145^{\circ}$  is converted by reduction into a *triamidonaphthol*, the hydrochloride of which crystallises in long, colourless needles; this salt readily oxidises in the presence of free acid, and is converted by ferric chloride into 2:3'-diamido-1:4-naphthaquinonimide, which crystallises in orange-red needles. The *hydrochloride*,  $\text{C}_{10}\text{H}_{14}\text{N}_3\text{OCl}_3 + \text{H}_2\text{O}$ , is readily soluble in water, and forms dark brown needles, whilst the *platinochloride* crystallises in very sparingly soluble, almost black, needles.

A. H.



**Chromotropic Acid.** By LUDWIG HANTOWER and ERNST TÄUBER (*Ber.*, 1898, 31, 2156—2159).—Phenylazochromotropic acid (chromotropic acid =  $C_{10}H_4(OH)_2(SO_3H)_2$  [ $= 1 : 1' : 3 : 3'$ ]), which the dye-works' chemists regard as a 2-azo-compound, is that in reality, for when it is reduced with stannous chloride, it yields an amidochromotropic acid that must be a 2-amido-compound, because oxidation with cooled concentrated nitric acid converts it into an acid that is characterised by its reaction with orthotolylenediamine (it forms a *tolyldihydroxynaphth-azinedisulphonic acid*) as 1'-hydroxy-1:2-naphthaquinone-3 : 3'-disulphonic acid. The sodium salts of these two acids were prepared; they are respectively brown and golden-yellow in colour. C. F. B.

**Ethereal Oils.** By SCHIMMEL and Co. (*Chem. Centr.*, 1898, i, 258—259; from Schimmel and Co.'s *Bericht*, 1897, October).—Malabar cardamoms oil, prepared from *Elettaria cardamomum* Matton, which yields 2.14 per cent., is soluble in 4 parts of 70 per cent. alcohol, has a sp. gr. = 0.943 at 15°, a rotatory power at 19° = +34° 52' (100 mm. tube), and a saponification number = 132. The oil contains cineol, a solid terpeneol of rotatory power = +83° 31' at 21°, and considerable quantities of alkylic acetates. Siam cardamoms oil is a semi-solid oil, obtained from *Ammomum cardamomum* L., which yields 2.4 per cent., is soluble in 1.2 parts of 80 per cent. alcohol, has a sp. gr. = 0.905 at 42°, a rotatory power at 42° = +38° 4', and a saponification number = 18.8. The acetyl derivative has a saponification number = 77.2. The oil contains dextroborneol and dextrocamphor. Cameroon cardamoms oil, prepared from *Ammomum angustifolium* Sonnerat, which yields 2.33 per cent., is soluble in 7—8 parts of 80 per cent. alcohol, has a sp. gr. = 0.907 at 15°, and a rotatory power = -20° 34'. It contains large quantities of cineol, and cannot be used as a substitute for Ceylon cardamoms oil. Oil of grains of Paradise, obtained from *Ammomum Melegueta* Roscoe, which yields 0.75 per cent., is soluble in 10—11 parts of 90 per cent. alcohol, has a sp. gr. = 0.894 at 15°, and a rotatory power = +3° 58'.

Fir oil, obtained from the needles of *Pinus sylvestris* L., dissolves in 8 parts of 90 per cent. alcohol with faint opalescence, has a sp. gr. = 0.884 at 15°, a rotatory power at 18° = -24° 8', and a saponification number = 34.8, which corresponds with a content of 12.1 per cent. of bornylic acetate. Hemlock oil, from the needles of *Abies canadensis* L., is soluble in equal parts of 90 per cent. alcohol, has a sp. gr. = 0.911 at 15°, a rotatory power = -25° 22' at 16°, and contains 38 per cent. of bornylic acetate. Spruce oil, from the needles of *Picea nigra* L. (or *alba*?), is soluble in half its volume of 90 per cent. alcohol, has a sp. gr. = 0.913 at 15°, a rotatory power = -23° 50' at 18°, and contains 38.1 per cent. of bornylic acetate. The two preceding oils, which both contain levorotatory pinene and levorotatory bornylic acid, cannot be distinguished from each other.

Dalmatian oil of rosemary is obtained by distilling the leaves, which yield 1.4—1.75 per cent., has a sp. gr. = 0.904—0.913 at 15°, a rotatory power varying from +4° 16' to 8° 52', and contains pinene and camphene. Two samples of the oil contained 5—6 per cent. of bornylic acetate and 17—19 per cent. of borneol. Oil of rosemary

should be dextrorotatory, have a sp. gr. greater than 0.9 at 15°, and dissolve in half a part of 90 per cent. alcohol, or in 10 parts of 80 per cent. alcohol. When one-tenth of its volume is distilled off, the distillate should be dextrorotatory.

The following new oils, obtained by distilling the plants, are also described. Oil of pepperwort, prepared from flowering *Satureja hortensis*, which yields 0.097 per cent., is soluble in 9 parts of 80 per cent. alcohol, has a sp. gr. = 0.904 at 15°, a rotatory power = +0° 4', and contains 38 per cent. of carvacrol. The oil from *Satureja montana*, which yields 0.18 per cent., is soluble in 4.5 parts of 70 per cent. alcohol, has a sp. gr. = 0.939 at 15°, a rotatory power = -2° 35', and contains 65 per cent. of phenols which consist principally of carvacrol. Xanthorrhæa resin oil, from the yellow Australian resin of *Xanthorrhæa hastilis* R. Br., which yields 0.37 per cent., has an odour like storax, a sp. gr. = 0.937 at 15°, a rotatory power = -3° 14', a saponification number = 74.3, an acid number = 4.9, an etherification number = 69.4, and contains styrene. The saponified oil boils at 145—240° (compare Hildebrand, *Arch. Pharm.*, 234, 698). Balsam oil is prepared from the flowering plant of *Tanacetum balsamita* L., which yields 0.064 per cent., has an odour of tansy, a sp. gr. = 0.943 at 15°, a rotatory power = -53° 48' at 16°, and boils at 207—283°. Larch oil, from the needles of *Larix europæa* D.C., which yields 0.22 per cent., is soluble in 5 parts of 90 per cent. alcohol, has a sp. gr. = 0.878 at 15°, a rotatory power = +0° 22' at 18°, a content of alkylic salt corresponding with 8.1 per cent. of bornylic acetate, and a content of alcohol corresponding with 6.14 per cent. of borneol; 70 per cent. of the oil distils at 160—180°.

When terpineol is heated with sodium acetate and acetic anhydride for 45 minutes, 84 per cent. of terpenylic acetate is obtained; by prolonging the action for 2 hours, the yield is reduced to 78 per cent. In reply to Erdmann and Huth (*J. pr. Chem.*, 1897, [ii], 56, 1), the authors would abolish the term rhodinol, which is used both for citronellol and for a mixture of citronellol and geraniol, and they state also that geraniol free from chlorine can be obtained by preparing the calcium chloride compound and shaking the oil liberated from it with warm water. The suggestion that the firm's commercial geraniol contains either chlorine compounds of higher boiling points and disagreeable odour or citronellol is also repudiated. E. W. W.

**Ethereal Oil of Angostura Bark.** By HEINRICH BECKURTS and JULIUS TROEGER (*Arch. Pharm.*, 1898, 236, 392—408. Compare Abstr., 1898, i, 37, 202).—The authors have endeavoured, without success, to again isolate the substance previously called by them "galipene alcohol." The amount of alcohol in the raw oil is, as shown by the acetyl value, about 14 per cent.

The right-handed terpene "galipene" (rotation in 100 mm. tube = +18°, and not  $[\alpha]_D = +18^\circ$  as previously stated) is not originally present in the oil, but is probably a product of inversion.

The left-handed sesquiterpene was extracted from the hydrobromic acid additive product of the raw oil on treatment with aniline, and, although it could not be obtained in a pure state, appears to

be cadinene. This conclusion was arrived at from the consideration of its physical constants, and the properties of its hydrochloride, hydrobromide, and hydriodide.

The inactive sesquiterpene (b. p. 255—260°), isolated previously from an inactive portion of the oil, shows some resemblance to caryophyllene, and the authors propose to call it "galipene," a name which they formerly gave to the right-handed terpene. With hydrobromic acid, it gives an oily, unstable additive product.

Acetic anhydride has no inverting action on either cadinene or the inactive terpene, and, therefore, the formation of the right-handed terpene is not due to this cause. The raw, left-handed oil is, however, inverted by simple distillation, and hydrobromic acid seems to convert the right-handed terpene into the left-handed cadinene. A. W. C.

**Acids in Essence of Geranium.** By JULIAN FLATAU and H. LABBÉ (*Compt. rend.*, 1898, 126, 1876—1879).—Indian essence of geranium contains no free acid, but when boiled with alcoholic potash it yields geraniol and an acid,  $C_{14}H_{28}O_2$ , which melts at 28.2°, and seems to be an isomeride of myristic acid. The silver, barium, calcium, and cupric salts were analysed; the first melts and decomposes at 191—192°, and the last contains  $1H_2O$ , and melts at 74—75°. The Indian essence also contains small quantities of acetic and butyric acids.

Bourbon essence of geranium contains some free acid, and when treated with alcoholic potash yields an acid,  $C_{10}H_{18}O_2$ , the silver salt of which melts and decomposes at 158°. The Bourbon essence also contains some acetic acid and a small quantity of valeric acid.

C. H. B.

**"Oil of Petit Grain."** By JACQUES PASSY (*Bull. Soc. Chim.*, 1897, [iii], 17, 519. Compare Semmler and Tiemann, *Abstr.*, 1892, 868).—In addition to the substances isolated by Semmler and Tiemann, the author also has found geraniol in oil of petit grain. J. J. S.

**Terpenes and Ethereal Oils. Fenchone.** By OTTO WALLACH [and M. HERTZ] (*Annalen*, 1898, 302, 371—387. Compare *Abstr.*, 1898, i, 486).—When lævorotatory fenchylic alcohol, prepared by reducing *d*-fenchone, is treated with phosphorus pentachloride, and hydrogen chloride removed from the product by the action of bases, the hydrocarbon fenchene,  $C_{10}H_{16}$ , is obtained. It has been hitherto supposed that this terpene is an individual substance, but finding that certain specimens on oxidation yielded hydroxyfenchenic acid melting at 138—139°, instead of at 152—153° (compare *loc. cit.*), the author has submitted the matter to investigation. As a result, it appears that fenchylic alcohol gives rise to two fenchylic chlorides, and these to two fenchenes, one dextrorotatory, and the other lævorotatory; as both are derived from dextrorotatory fenchone, the author distinguishes them as *Dd*-fenchene and *DL*-fenchene, respectively.

The rotation of fenchylic chloride, prepared from *DL*-fenchylic alcohol, has been observed to vary between the limits  $\alpha_D = -13^\circ$  and  $\alpha_D = +5.1^\circ$ , in a 1-decimetre tube; the direct product is lævorotatory, but the subsequent treatment modifies the rotatory power to a degree which has not been exactly determined. Strongly lævorotatory fen-

chylic chloride gives rise to *l*-fenchene; feebly laevorotatory, or nearly inactive chloride, however, yields *d*-fenchene, the observed limits of rotation for these two hydrocarbons being  $\alpha_D = \pm 21^\circ$  in a 1-decimetre tube. In order to obtain *d*-fenchene, it is necessary to employ fenchylic chloride which has not been distilled, and *l*-fenchene is prepared by heating *d*-fenchene with alcoholic sulphuric acid during several hours, and may be also obtained by fractional oxidation with potassium permanganate. Whilst *Dl*-fenchene is attacked but slowly by a 3 per cent. solution of potassium permanganate, yielding the hydroxyfenchenic acid already described (*loc. cit.*, 488), *Dd*-fenchene is oxidised in a few minutes.

*Dl*-Hydroxyfenchenic acid crystallises from dilute acetone in leaflets melting at  $152\text{--}153^\circ$ ; it has the specific rotatory power  $[\alpha]_D = -56.8^\circ$ .

*Dd*-Hydroxyfenchenic acid crystallises from dilute acetone in well-formed, transparent prisms and melts at  $138\text{--}139^\circ$ ; it has the specific rotatory power  $[\alpha]_D = +7.69^\circ$ .

*Ld*-Hydroxyfenchenic acid, prepared from *l*-fenchone, melts at  $152\text{--}153^\circ$ , and has the specific rotatory power  $[\alpha]_D = +57.3^\circ$ ; the racemic hydroxyfenchenic acid melts at  $142\text{--}143^\circ$ .

Fenchylic chloride is slowly oxidised by potassium permanganate, yielding *Dl*-hydroxyfenchenic acid, and is produced when hydrogen chloride is passed into a solution of fenchene in glacial acetic acid.

*Dd*-Fenchocamphorone, obtained by oxidising *Dl*-hydroxyfenchenic acid (*loc. cit.*), melts at  $109\text{--}110^\circ$ , and has  $[\alpha]_D = +14.64^\circ$ ; the oxime has  $[\alpha]_D = -50.30^\circ$ , and the semicarbazone, which melts and effervesces at  $210\text{--}212^\circ$ , has  $[\alpha]_D = -131.3^\circ$ .

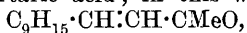
*Dl*-Fenchocamphorone, obtained by oxidising *Dd*-hydroxyfenchenic acid, melts at  $62\text{--}63^\circ$ , and boils at  $201\text{--}202^\circ$ ; it is very volatile, and has  $[\alpha]_D = -16.69^\circ$ . The oxime melts at  $54\text{--}56^\circ$ , and has  $[\alpha]_D = +49.03^\circ$ , whilst the semicarbazone, which crystallises in prisms melting at  $204\text{--}206^\circ$ , has  $[\alpha]_D = +58.11^\circ$ .

From these results, the author draws the important conclusion that an ethylenic linkage, occurring in two stereoisomeric substances, does not in each case exhibit the same degree of stability towards potassium permanganate.

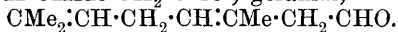
M. O. F.

**Lemon-grass Oil.** By W. STIEHL (*J. pr. Chem.*, 1898, 58, 51—101).—By carefully distilling 50 kilos. of lemon-grass oil with steam, and collecting the distillate in separate fractions, cymene,  $\alpha$ -limonene, and dipentene were detected, but neither geraniol nor citronellal. The bulk of the oil consisted of a mixture of aldehydes, which it was not found possible to separate satisfactorily by distillation under diminished pressure. The following method, or modifications of it, was consequently adopted. The mixture of aldehydes of lemon-grass oil (1 part) is shaken with a 35 per cent. solution of sodium hydrogen sulphite (2 parts) and water (2 parts) until the crystals that form at first have disappeared. Allolemonal (*l*-licarhodol, Barbier and Bouveault, *Abstr.*, 1896, i, 311, 345) is then present as an oil, and is removed; the aqueous solution yields no aldehydes when treated with sodium carbonate in the cold, but when it is shaken with strong caustic soda, citriodor-aldehyde (Dodge, *Abstr.*, 1891, 285)

separates as an oil. If, however, when the mixture of aldehydes is shaken with the sulphite solution, precautions are taken to keep the temperature low until the crystalline compound has been formed, after which the temperature is allowed to rise to about 45—50°, and the mixture is then left in a cool place for 24 hours, crystals are obtained which yield geranial (or citral: Semmler, Abstr., 1891, 539) when they are freed from oil and decomposed with sodium carbonate solution at 45°. The method of separation depends on the fact that all three aldehydes form compounds of the usual type with sodium hydrogen sulphite in the cold; this reaction is attended with the development of heat, and the consequent rise of temperature, if it be not prevented, effects the decomposition of the allolemonal compound (which takes place at about 60° in aqueous solution) and converts the citriodor-aldehyde compound into a compound with 2 mols. of sodium hydrogen sulphite (decomposed by aqueous sodium carbonate only on heating, although by caustic soda in the cold), and the geranial compound into a true sulphonate (which is not decomposed, even by caustic soda). This behaviour of citriodor-aldehyde resembles that of cinnamaldehyde (Heusler, Abstr., 1891, 1052); hence the former also may be assumed to contain the grouping  $\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$ . The semicarbazones (Thiele and Stange, Abstr., 1894, i, 165) and  $\beta$ -naphthocinchonic acid derivatives (Doebner, Abstr., 1895, i, 261) of these three aldehydes were prepared; except in the case of allolemonal, the crude semicarbazones could be separated by fractional crystallisation from methylic alcohol into two modifications; these were not obtained pure in the case of citriodor-aldehyde semicarbazone. The aldehydes,  $\text{C}_9\text{H}_{15}\cdot\text{CHO}$ , were mixed at 0° with excess of acetone, alcoholic sodium ethoxide was added gradually, and, after a short interval, aqueous tartaric acid; in this way, ketones,



were obtained, respectively citriodorylidene-acetone, allolemonylidene-acetone, and geranylidene-acetone; of these, the last is identical with Tiemann's pseudoionone, whilst the first two correspond respectively to his hypothetical violet-ketones, II and I (*Ber.*, 1898, 31, 811, 853); the semicarbazone of each was prepared. The properties of these compounds are tabulated at the end of the abstract. For the aldehydes themselves, the following formulæ are adopted: citriodor-aldehyde,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CHO}$ ; allolemonal,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$ ; geranial,



The proportions of the substances found in a genuine sample of lemon-grass oil were: hydrocarbons, 12—50; citriodor-aldehyde, 40—50; allolemonal, 25—30; geranial, 8—10 per cent. Probably, the geranial was formed by the action of the sodium hydrogen sulphite, and does not exist in the original oil at all; if the oil is treated with acid agents, a large yield of geranial (citral) is obtained, for the citriodor-aldehyde and allolemonal are converted by acids, more or less completely, into geranial.

It follows from the composition of lemon-grass oil thus ascertained that the "artificial oil of violets" prepared from it cannot be identical (compare Doebner, Abstr., 1898, i, 676) with the ionone pre-

pared by Tiemann's method from citral (geranial); it must be a mixture of this substance with Tiemann's two hypothetical "violet-ketones." Nor can calcium hydroxide act as the condensing agent in its formation, for the three aldehydes in question, as also their compounds with acetone, are decomposed by alkalis.

	Citriodor- aldehyde.	Allolemonal ( <i>l</i> -licarhodol).	Geranial (citral).
Boiling point under 12 mm. ....	108—109°	117·5—119°	111—112°
" " at 20° " 760 " .....	228—229°	233—235°	225—227°
Sp. gr. at 20° .....	0·8883	0·9017	0·8868
Index of refraction $n_D$ at 20° .....	1·48538	1·48316	1·48752
Rotation $\alpha_D$ per 1 dm. ....	$\pm 0^\circ$	$-5^\circ 6'$	$\pm 0^\circ$
Melting point of semicarbazone ...	134°	169°	141°
" " $\alpha$ -semicarbazone...	?	—	160° (plates)
" " $\beta$ - " .....	?	—	150° (needles)
" " naphthocinchonic compound.....	204°	235°	197°

Products of Condensation with Acetone.

Boiling point under 12 mm. ....	149—152°	157—159°	143—145°
Sp. gr. at 20° .....	0·8980	0·9000	0·9037
Index of refraction $n_D$ at 20° .....	1·52903	1·53150	1·52736
Melting point of semicarbazone ...	110—112°	142—143°	134—135°

C. F. B.

**Conversion of Linalool into Terpeneol Melting at 35°.** By KARL STEPHAN (*J. pr. Chem.*, 1898, [ii], 58, 109—120).—Barbier's licarhodol (*Abstr.*, 1893, i, 544) was prepared by heating *l*-linalool with acetic anhydride for 8 hours (5 would suffice) at 150—160°, and shown to be a mixture of about 85 parts of geraniol with 15 of *d*-terpeneol. The presence of geraniol has been admitted already; as regards terpeneol, after 26 fractionations a fraction was obtained from which it crystallised out in a freezing mixture.

When linalool is heated with acetic acid, some *d*-terpeneol is formed also. In the cold, acetic acid has practically no action, but if to the solution of linalool in three times its weight of acetic acid  $\frac{1}{2}$  per cent. of sulphuric acid be added and the temperature kept below 20°, about 45 per cent. is converted into *d*-terpeneol and 10 into geraniol; in light petroleum, instead of acetic acid, solution, the sulphuric acid has no such action. Formic acid acts violently on *l*-linalool, forming dipentene and terpinene; if, however, the temperature is kept below 20°, 50 per cent. of the linalool is converted into *d*-terpeneol. In a similar fashion, formic acid converts *d*-linalool (coriandrol) into *l*-terpeneol.

C. F. B.

**Bromocamphor.** By CHARLES MOUREU (*Bull. Soc. Chim.*, 1897, [iii], 17, 552—553).—The author has obtained a considerable amount of phosphorus tribromide by heating equivalent quantities of bromocamphor and of phosphoric anhydride at about 200°.

J. J. S.

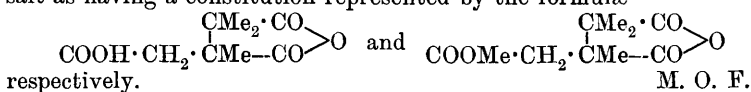
**Camphoronic Acid.** By OSSIAN ASCHAN (*Annalen*, 1898, 302, 51—76. Compare Bredt, *Abstr.*, 1898, i, 263).—Three structurally different anhydromcamphoronic acids are theoretically possible. The author describes experiments carried out with a view to ascertaining whether

more than one member of this group exists, but although the question cannot be regarded as finally settled, he considers that camphoronic acid yields the same anhydride by the following methods: 1, distillation; 2, heating at  $105^{\circ}$ ; 3, heating at  $200^{\circ}$ ; 4, action of acetic chloride on the dry acid at common temperatures; 5, action of acetic chloride on the acid suspended in boiling ether.

Methylic dihydrogen camphoronate, prepared by the action of sodium methoxide (2 mols.) on anhydrocamphoronic acid, and treatment of the product with sulphuric acid, crystallises from a small quantity of water in lustrous, flattened prisms or long needles; when plunged into a bath at  $120^{\circ}$ , it melts at  $141-142^{\circ}$ , but is identical with the compound described by Bredt (Abstr., 1895, i, 242). The difference in melting point arises from the manner in which the two specimens were heated.

Two methylic anhydrocamphoronates have been described by Bredt (Abstr., 1895, i, 242), and although the salts are not interconvertible by the action of heat, both are produced when methylic iodide acts on sodium or silver anhydrocamphoronate. The *sodium* salt of anhydrocamphoronic acid is a lustrous, crystalline substance, and the *silver* salt forms microscopic leaflets; the sodium salt, when heated with methylic iodide at  $135-140^{\circ}$ , and the silver salt on the water-bath, are both of them converted into a mixture of  $\alpha$ - and  $\beta$ -methylic anhydrocamphoronates. In order to explain this fact, it is necessary to suppose that the anhydride ring in anhydrocamphoronic acid is labile, and, undergoing rearrangement, yields a second ethereal salt, structurally isomeric with the first.

The author regards anhydrocamphoronic acid and the  $\alpha$ -methylic salt as having a constitution represented by the formulæ



**Olibanum.** By ALEXANDER TSCHIRCH and HALBEY (*Arch. Pharm.*, 1898, 236, 487—503).—"Olibanum electum" is extracted with 90 per cent. alcohol, and the concentrated extract poured into water acidified with hydrochloric acid, when a clear, yellow resin is precipitated, and a bitter principle goes into solution. By repeating this process and distilling the residue with steam to get rid of an ethereal oil, the pure resin is obtained as a clear, yellow mass easily soluble in the ordinary organic solvents. When dissolved in ether and extracted with caustic soda, *boswellic acid*,  $\text{C}_{32}\text{H}_{52}\text{O}_4$ , is obtained as a white powder melting at  $150^{\circ}$ , and showing little tendency to crystallise. It can neither be acetylated nor benzoylated. The *sodium*, *potassium*, *barium*, and *copper* salts are described. The resin probably contains some boswellic acid in the form of an ethereal salt, and also *olibano-resen*,  $(\text{C}_{14}\text{H}_{22}\text{O})_n$ , a powder insoluble in sodium hydroxide and melting at  $62^{\circ}$ .

The portion of olibanum insoluble in alcohol consists principally of a gum containing magnesium, calcium, and arabic acid.

A tabulated list of the constituents of some drugs is given, and also of the behaviour of a large number of resinous substances towards the cholesterol reaction.

A. W. C.

**Action of Nitric Acid on Ouabain.** By ALBERT ARNAUD (*Compt. rend.*, 1898, **126**, 1873—1876).—When ouabain is treated with nitric acid of sp. gr. = 1.2, it is only partially oxidised, and no oxalic acid is formed, but hydrolysis takes place, and insoluble nitro-derivatives are produced. If a mixture of 100 grams of ouabain and 300 c.c. of the acid is heated to about 40° until the reaction begins, and the temperature developed is not allowed to exceed 75°, a nitro-derivative,  $C_{23}H_{24}(NO_2)_2O_6$ , is formed, and crystallises from acetone in yellowish, silky needles which melt and decompose at about 300°. It behaves as a dibasic acid; the potassium and sodium salts are crystallisable, and form intense orange-red, aqueous solutions; the calcium salt is similar, but less soluble; the ammonium salt forms golden-yellow needles.

If the action of the acid takes place at a temperature not exceeding 15°, a small quantity of another nitro-derivative,  $C_{23}H_{25}(NO_2)O_6$ , is obtained as well as the preceding compound. It is almost insoluble in all neutral solvents, but dissolves readily in alkalis, forming intense orange solutions, from which it is reprecipitated on the addition of excess of acid. It melts and decomposes at about 280°. The ammonium salt,  $C_{23}H_{24}(NO_2)O_6 \cdot NH_4$ , forms small, yellow prisms almost insoluble in water; the other salts are orange or orange-red.

Both nitro-derivatives are derived from the compound  $C_{24}H_{36}O_8$ , which results from the hydrolysis of ouabain, and which, in presence of nitric acid, is both oxidised and nitrated. C. H. B.

**Digitoxin and Digitalin.** By HEINRICH KILIANI (*Ber.*, 1898, **31**, 2454—2464).—Digitoxigenin has a molecular weight in naphthalene, as determined by Baumann-Fromm's method, of 405—412; the formula  $C_{22}H_{32}O_4$  requires 360.

*Digitoxoseoxime*,  $C_6H_{13}NO_4$ , obtained by treating digitoxose with hydroxylamine, crystallises in concentrically arranged groups of shining needles, is excessively soluble in water and alcohol, and melts at 102°; it no longer exhibits the blue coloration so characteristic of digitoxose on addition of ferric chloride. The air-dried crystals of the oxime change after several months to a yellow, gum-like mass. The *lactone* of digitoxosecarboxylic acid,  $C_7H_{12}O_5$ , made by mixing digitoxose with concentrated hydrocyanic acid and ammonia, is purified by preparing the barium salt of the acid, and is crystallised from 50 per cent. alcohol; it melts at 153—154°; *calcium digitoxosecarboxylate*,  $(C_7H_{13}O_6)_2Ca$ , prepared by boiling an aqueous solution of the pure lactone with calcium carbonate, contains 9.15 per cent. of calcium, a number which materially assists in the exclusion of the formula  $C_9H_{18}O_6$  for digitoxose.

The colour reactions of digitoxose, which are not exhibited by arabinose, rhamnose, dextrose, galactose, levulose, or sorbose, add probability to the view, already expressed by the author, that digitoxose is a cyclic compound, and in that case its formula,  $C_6H_{12}O_4$ , would indicate that a true carboxyl group is not present, but that two hydroxyl groups are attached to one carbon atom.

Analyses of digitoxin, and estimations of the digitoxigenin formed from it by hydrolysis, gave results which are in agreement with the



formula  $C_{34}H_{54}O_{11} (= C_{22}H_{32}O_4 + 2C_6H_{12}O_4 - H_2O)$ . Attempts to determine its molecular weight in acetic acid were found to be valueless, owing to the unavoidable decomposition of the substance.

*Anhydrodigitoxigenin*,  $C_{22}H_{30}O_3$ , is made by shaking digitoxigenin with five parts each of 95 per cent. alcohol and concentrated hydrochloric acid at the ordinary temperature, and then allowing the mixture to remain during 6 hours; the liquid is then diluted, and allowed to remain for another 6 hours, when the precipitate is separated, washed, and dried. It crystallises from dilute alcohol in nodular aggregates of colourless prisms, and sinters at  $210-220^\circ$ , according to the rate of heating. A determination of its molecular weight in naphthalene gave the value 351 (calculated = 342). It behaves exactly like the parent substance towards concentrated sulphuric acid containing iron; if the amount of acid be such that no coloration is at first produced, the gradual development of a beautiful red tint is noticed and simultaneously of a green fluorescence.

*Toxigenone*,  $C_{20}H_{26}O_3$  or  $C_{19}H_{24}O_3$ , is the name used by the author for a substance obtained by adding chromic acid mixture to a solution of anhydrodigitoxigenin in ten parts of hot acetic acid; it separates immediately in yellowish needles resembling sal-ammoniac. It is purified by dissolving it in chloroform, treating with blood-charcoal, and adding ether to the filtered liquid, when colourless, fern-like crystals separate. With concentrated sulphuric acid containing iron, a yellow coloration is gradually produced. When heated, it turns yellow at  $220^\circ$ , but does not melt even at  $250^\circ$ . Boiling dilute alkalis have no effect on the substance, which seems to be a ketone. Toxigenone is sparingly soluble in cold alcohol and acetic acid, but dissolves readily in concentrated sulphuric acid.

Digitaligenin has a molecular weight in naphthalene or acetic acid of 338—340, hence the earlier formulæ must be rejected, and one of the formulæ  $C_{23}H_{32}O_3$  or  $C_{22}H_{30}O_3$  probably represents its true composition. *Digitalose*,  $C_7H_{14}O_5$ , is the name suggested by the author for a sugar produced by the hydrolysis of digitalin; by treating the sugar mixture with bromine,  $\delta$ -gluconic acid may be obtained and digitalonic acid,  $C_7H_{14}O_6$ , hence it is probable that  $\delta$ -glucose and digitalose are products of hydrolysis of digitalin. Analysis of the calcium salt of digitalonic acid gave  $Ca = 9.35$  per cent. and it was noticed that the salt, dried at  $100^\circ$ , burned without any preliminary fusion, thus differing from the calcium salt of the metameric digitoxosecarboxylic acid. On the basis of the foregoing results, the authors conclude that digitalin has the composition  $C_{35}H_{56}O_{14}$  or  $C_{36}H_{58}O_{14} (= C_{22}H_{30}O_3$  or  $C_{23}H_{32}O_3 + C_6H_{12}O_6 + C_7H_{14}O_5)$ . Molecular weight determinations of digitalin in glacial acetic acid gave very uncertain results.

Digitaligenin, when oxidised in acetic acid solution with chromic acid mixture, yields a substance, insoluble in water, which crystallises from alcohol, and appears to be identical with toxigenone.

The properties of French "digitaline cristallisée" correspond in many respects with those of the German preparations of "digitoxin," but certain marked differences between them are observable. Thus, analyses of the anhydrodigitoxigenins prepared from each indicate

that the French substance contains an additional  $-\text{CH}_2-$  group; the French glucoside, deposited from its solution in chloroform, is at first amorphous and requires a temperature of  $40^\circ$  for its hydrolysis with alcoholic hydrogen chloride, whilst digitoxin separates from chloroform in a crystalline form, and is hydrolysed at the ordinary temperature with the foregoing agent. Again, the crystals of "digitaline crystallisée" show extinction parallel to their longest sides, whilst those of digitoxin, prepared under like conditions, extinguish when their longest sides make an angle of  $14^\circ$  with the plane of polarisation; for this reason and for several others, Prof. Groth pronounces them to be distinct substances. A. L.

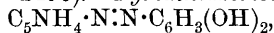
**Gelsemic Acid.** By ERNST SCHMIDT (*Arch. Pharm.*, 1898, 236, 324—328).—Wormley (*Chem. Centr.*, 1870, 678) obtained a substance from the root of "*Gelsemium sempervirens*" which he called "gelsemic acid," and was said to be æsculin by Robbins (this Journ., 1877, ii, 344). Later, Virgil Coblentz (*Amer. J. Pharm.*, 1897) stated that gelsemic acid has the formula  $\text{C}_{13}\text{H}_9\text{O}_3(\text{OH})_2$ . Some time since, the author had reason to believe that gelsemic acid was identical with  $\beta$ -methyl-æsculetin, a supposition which he now proves to be correct by showing that these two substances have the same melting point ( $202-203^\circ$ ), appearance, and solubility. Both contain one methoxyl-group as shown by Zeisel's method, and, on treatment with hydriodic acid, give æsculetin,  $\text{C}_9\text{H}_6\text{O}_4$ , crystallising from ethylic acetate in slender, white glistening needles which do not melt when heated to  $250^\circ$ .

Gelsemic acid must, therefore, be struck out of chemical literature. A tabulated comparison of the properties of gelsemic acid and  $\beta$ -methylæsculetin, and of the substance,  $\text{C}_9\text{H}_6\text{O}_4$ , obtained by the action of hydriodic acid on gelsemic acid and æsculetin, is given.

A. W. C.

**Hydrazo- and Azo-compounds of the Pyridine Series.** By WILHELM MARCKWALD (*Ber.*, 1898, 31, 2496—2497).—The  $\alpha$ - and  $\gamma$ -chloro-derivatives of pyridine and quinoline readily react with hydrazine at about  $150^\circ$ . Thus 4-chloro-2:6-dimethylpyridine is converted by hydrazine hydrate at  $150^\circ$  into 4-lutidylhydrazine, [2:6-dimethylpyridine-4-hydrazine],  $\text{NH}_2\cdot\text{NH}\cdot\text{C}_5\text{NH}_2\text{Me}_2$ , which forms white crystals, and melts at  $115-116^\circ$ . Phenylhydrazine behaves in a similar manner, giving rise to a hydrazo-derivative which is converted by oxidation into an azo-compound. Further details will be given in a future communication. A. H.

**$\beta$ -Diazopyridine and  $\beta$ -Diazoamidopyridine.** By ERNST MOHR (*Ber.*, 1898, 31, 2495—2496).—*Pyridineazoresorcinol*,



prepared from diazotised  $\beta$ -amidopyridine and resorcinol, crystallises in transparent, brown plates or prisms with violet reflex, becoming darker at  $190^\circ$ , finally melting at  $218^\circ$ .

$\beta$ -Diazoamidopyridine,  $\text{C}_5\text{NH}_4\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_5\text{NH}_4$ , obtained by the action of sodium nitrite on  $\beta$ -amidopyridine hydrochloride, crystallises from benzene in pale yellow needles with violet reflex; it melts and evolves gas at  $173-174^\circ$ .

*Benzylidene-β-pyridylhydrazine*,  $C_5NH_4 \cdot NH \cdot N : CHPh$ , is prepared by reducing diazotised amidopyridine with tin and hydrochloric acid, and treating the hydrazine with benzaldehyde; it crystallises from dilute alcohol in aggregates of needles, and melts at  $163-164^\circ$ .

M. O. F.

**Formation of Condensed Nuclei with Para-linkings.** By RICHARD STOERMER (*Ber.*, 1898, 31, 2541—2543).—The *hydrochloride* of piperidoaldehyde,  $C_7H_{14}ONCl$ , is made by heating the corresponding acetal (*Abstr.*, 1894, i, 556, and 1895, i, 479) with a large excess of hydrochloric acid which is afterwards removed in a vacuum; the salt, obtained by triturating the syrupy residue with ether, forms white crystals, and melts at  $103^\circ$ . The *platinochloride* crystallises in orange-yellow needles and melts at  $121-122^\circ$ ; the *aurochloride* forms small, yellow crystals and melts at  $109-111^\circ$ . The free base,  $C_5H_{10} \cdot N \cdot CH_2 \cdot CHO$ , may be crystallised from ether; it dissolves readily in alcohol and ether, and sparingly in water; it decomposes quickly in the free state. All attempts to cause internal condensation with elimination of water resulted in the resolution of the substance into piperidine and acetaldehyde. The *oxime*,  $C_7H_{14}O_2N_2$ , is obtained in white, flocculent masses, dissolves readily in alcohol and water, is insoluble in ether and chloroform, and melts at  $135-136^\circ$ ; possibly it has the constitution  $C_5H_{10} : NH \langle \underset{O}{\underset{|}{CH_2 \cdot CH}} \rangle N$ . The *semicarbazone* crystallises well, is a powerful base, and melts at  $76^\circ$ .

A. L.

**Conversion of Nicotinic Acid into β-Amidopyridine.** By THEODOR CURTIUS and ERNST MOHR (*Ber.*, 1898, 31, 2493—2495).—Nicotinic *hydrazide*,  $C_5NH_4 \cdot CO \cdot NH \cdot NH_2$ , prepared from ethylic nicotinate and hydrazine hydrate, dissolves readily in water and in alcohol, but sparingly in benzene; it melts at  $158-159^\circ$ , and reduces Fehling's solution. The *hydrochloride* and *benzylidene* derivative melt at  $227^\circ$  and  $149-152^\circ$  respectively.

*Nicotinazide*,  $C_5NH_4 \cdot CO \cdot N_3$ , obtained by the action of sodium nitrite on the hydrochloride of nicotinic hydrazide, separates from ether as a white, crystalline mass with pungent odour, and melts at  $47-48^\circ$ . When the ethereal solution is heated with absolute alcohol in a reflux apparatus, *β-pyridylurethane*,  $C_5NH_4 \cdot NH \cdot COOEt$ , is produced; it crystallises from petroleum in aggregates of long, slender needles, and melts at  $86-87^\circ$ .

*Di-β-pyridylcarbamide*,  $CO(NH \cdot C_5NH_4)_2$ , is formed when nicotinazide is agitated with hot water until nitrogen ceases to be evolved; it crystallises from alcohol in groups of four-sided prisms, and melts at  $217^\circ$ , evolving gas.

*β-Amidopyridine hydrochloride* is produced when *β-pyridylurethane* is heated with fuming hydrochloric acid in a reflux apparatus, or when *di-β-pyridylcarbamide* is heated with the same agent, in a sealed tube, at  $125^\circ$ ; the *platinochloride*, when crystallised from concentrated hydrochloric acid, has the composition  $(C_5H_6N_2)_2, H_2PtCl_6 + 2HCl$ , and blackens and intumesces at  $239^\circ$ .

M. O. F.

**Action of Alkylid Iodides on  $\alpha$ -Methylindole in Alkaline Media.** By ANTONIO PICCININI (*Gazzetta*, 1898, 28, ii, 87—90).—On warming a mixture of  $\alpha$ -methylindole with 20 per cent. potash and methylic iodide at  $40^\circ$  for 12 hours, the so-called pentamethyldihydroquinoline of Zatti and Ferratini (*Abstr.*, 1892, 614) is obtained; on interrupting the operation, after three hours heating, the trimethylated base is obtained.

If ethylic iodide is used in place of methylic iodide, no pentethylated product is formed, but the bases,  $C_{13}H_{17}N$  and  $C_{13}H_{16}NEt$ , described by Plancher (*Abstr.*, 1898, i, 536). W. J. P.

**Behaviour of Dihydro- $\alpha$ -methylindole on Reduction with Hydrogen Iodide.** By ANTONIO PICCININI and G. CAMOZZI (*Gazzetta*, 1898, 28, ii, 91—100).—In order to prepare an octohydro-compound, the authors heated dihydro- $\alpha$ -indole with hydriodic acid and red phosphorus at  $240^\circ$  for 12 hours, but found that opening of the indole ring had occurred, with formation of *orthopropylaniline*,  $C_9H_{13}N$ ; the new base is a colourless oil of aromatic odour boiling at  $219^\circ$ , and gives the isonitrile reaction. The *picrate*,  $C_9H_{13}N \cdot C_6H_2(NO_2)_3 \cdot OH$ , crystallises in yellow needles melting at  $151^\circ$ , and the *hydrochloride*,  $C_9H_{13}N \cdot HCl$ , in colourless needles melting at  $173^\circ$ ; the base yields a diazo-compound with nitrous acid.

Orthopropylacetanilide,  $C_9H_{12}N \cdot Ac$ , crystallises in colourless needles melting at  $104$ — $105^\circ$ , and orthopropylbenzanilide in colourless prisms melting at  $119^\circ$ . W. J. P.

**Indigotin.** By LEO MARCHLEWSKI and L. G. RADCLIFFE (*J. pr. Chem.*, 1898, [ii], 58, 102—109).—This paper describes a more exact study of some reactions first described by O'Neill (*Mem. Manchester Phil. Soc.*, 1892), since deceased. When finely-powdered indigotin is dissolved in acetic acid, oxidised by the gradual addition of finely-powdered potassium permanganate, and washed with acetic acid, first pure and then containing sulphurous anhydride, a product is obtained which is insoluble in all ordinary solvents in the cold, decomposes when heated, and appears to be *diacetoxyindigotin*,  $C_2(OAc)_2 \left[ \begin{array}{c} <CO> \\ | \\ NH \end{array} C_6H_4 \right]_2$ . Boiling with water decomposes it into acetic acid, isatin, and indigotin; when treated with caustic soda in the cold, it yields sodium acetate, indigotin, and *di-isatinic acid*,  $C_{16}H_{14}N_2O_6$ , which melts at  $226$ — $227^\circ$ , loses  $2H_2O$  when heated at  $115^\circ$ , forms a *silver salt*,  $C_{16}H_{11}AgN_2O_5$ , and a *bromo-derivative*,  $C_{16}H_{12}Br_2N_2O_6$ . C. F. B.

**Derivatives of Lepidine.** By WILHELM KOENIGS (*Ber.*, 1898, 31, 2364—2376).—*Dibromonitrolepidine*, obtained by brominating nitrolepidine in glacial acetic acid in the presence of fused sodium acetate at  $100^\circ$ , separates from ether or from benzene and petroleum in colourless crystals and melts at  $114$ — $115^\circ$ . *Nitro-4'-quinolinealdehyde*, prepared by warming the dibromide with silver acetate in 60 per cent. acetic acid, melts at  $175^\circ$ , and crystallises from petroleum and benzene as a yellow powder.

*Tribromonitrolepidine* results from the action of excess of bromine on nitrolepidine; it forms lustrous crystals and melts at  $162^{\circ}$ ; when heated with lead acetate in glacial acetic acid solution, it is converted into an acid which does not contain bromine. These results show that in both the di- and tri-bromonitrolepidines all the bromine atoms are in the side chain, and that their constitutions may be thus represented,  $\text{NO}_2 \cdot \text{C}_9\text{NH}_6 \cdot \text{CHBr}_2$  and  $\text{NO}_2 \cdot \text{C}_9\text{NH}_6 \cdot \text{CBr}_3$ ; the monobromo-derivative has not yet been obtained. 4'-*Quinolylethanol* (*lepidinealkine*; 4-hydroxyethylquinoline),  $\text{C}_9\text{NH}_6 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , is formed when lepidine is heated in sealed tubes at  $100^{\circ}$  with its own weight of 20 per cent. formaldehyde; it can be purified by means of its *picrate*, which crystallises in yellow needles and melts at  $155\text{--}157^{\circ}$ . The *hydrochloride* is colourless and melts at  $146^{\circ}$ ; the *platinochloride*,  $(\text{C}_{11}\text{H}_{11}\text{NO})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms yellowish-red crystals and melts at  $202^{\circ}$ . The free base has not been obtained crystalline.

4'-*Quinolylpropanediol*,  $\text{C}_9\text{NH}_6 \cdot \text{C}_3\text{H}_5(\text{OH})_2$ , is produced when twice as much formaldehyde is employed as in the former experiment; the free base crystallises from ethylic acetate in colourless plates which melt at  $127\text{--}129^{\circ}$ ; it is soluble in the ordinary solvents, and separates from its aqueous solution in slender needles. The *hydrochloride* crystallises from alcohol and melts at  $172^{\circ}$ . The *platinochloride* crystallises with  $2\text{H}_2\text{O}$  and melts at  $200\text{--}202^{\circ}$ ; the *picrate* melts at  $170\text{--}172^{\circ}$ . Quinolylpropanediol yields cinchonic acid on oxidation with nitric acid or sodium hypobromite; when heated at  $190^{\circ}$  under diminished pressure, it gives off gas, and a sublimate of trioxymethylene is obtained. The *monobromhydrin*, obtained when quinolylpropanediol, is warmed with concentrated hydrobromic acid, crystallises from benzene in colourless plates and melts at  $126\text{--}127^{\circ}$ . When heated at  $100\text{--}110^{\circ}$ , or when boiled with alcohol or benzene, it is converted into the soluble hydrobromide of a base which does not contain bromine.

4'-*Quinolylpropanedioldi-iodohydrin hydriodide*, produced on boiling together quinolylpropanediol, hydriodic acid, and red phosphorus, crystallises in golden-yellow needles, and melts and decomposes at  $188^{\circ}$ . The free *di-iodohydrin* is colourless, and melts and decomposes at  $140^{\circ}$ . The *moniodohydrin*, obtained from the mother liquor of the preceding compound, separates from its solutions in ether and ethylic acetate in colourless crystals, and melts at  $117\text{--}119^{\circ}$ .

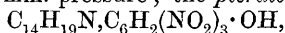
4'-*Propylquinoline* results from the action of fuming hydriodic acid and red phosphorus on quinolylpropanediol at  $160^{\circ}$ . The *platinochloride* crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$  and melts and decomposes at  $204^{\circ}$ ; the *picrate* crystallises from alcohol in yellow needles and melts at  $172\text{--}173^{\circ}$ . The double chlorides of gold, mercury, cadmium, and zinc are precipitated in an oily form at first, but become crystalline on standing. The *methiodide*, which forms yellow crystals easily soluble in water, melts at  $173^{\circ}$ .

With the object of establishing the constitution of the quinolylpropanediol, the reduction of chloral-lepidine was studied. When treated with red phosphorus and fuming hydriodic acid at  $160^{\circ}$ , this substance yields an oily 4'-*propylquinoline*, which should have the constitution  $\text{C}_9\text{NH}_6 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ ; the *platinochloride* of this substance melts  $8^{\circ}$  lower than the corresponding salt of the preceding base, and

also differs from it in containing no water of crystallisation. The *picrate* of this base melts at  $198^\circ$ , that of the preceding base at  $173^\circ$ .

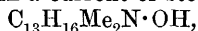
Quinolypropanediol may have either of the following constitutions,  $4\text{-C}_9\text{NH}_6\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , or  $4\text{-C}_9\text{NH}_6\cdot\text{CH}(\text{CH}_2\cdot\text{OH})_2$ , according as to whether the above propylquinolines are alike or different.  
G. T. M.

**Preparation and Properties of Pentamethyldihydroquinoline from Indoles.** By ANTONIO PICCININI (*Gazzetta*, 1898, 28, ii, 40—51).—The most convenient method of preparing the pentamethyldihydroquinoline of Zatti and Ferratini (*Abstr.*, 1892, 614) is by treating trimethyl- or tetramethyl-dihydroquinoline with potash and methylic iodide in aqueous solution at about  $40^\circ$ ; after distilling off the excess of methylic iodide, the base is purified by ether, conversion into sulphate and distillation in a current of steam. The base distils at  $171\text{--}172^\circ$  under 46 mm. pressure, and in a current of hydrogen at  $268\text{--}269^\circ$  under 750 mm. pressure; the *picrate*,



crystallises in golden scales melting at  $128\text{--}129^\circ$ , and the *hydriodide* in colourless prisms melting at  $178\text{--}179^\circ$ . The *aurichloride*,  $\text{C}_{14}\text{H}_{19}\text{N}\cdot\text{HAuCl}_4$ , crystallises in long needles melting and decomposing at  $152\text{--}153^\circ$ .

On heating pentamethyldihydroquinoline with methylic iodide at  $100^\circ$ , it yields the methiodide,  $\text{C}_{15}\text{H}_{22}\text{NI}$ , which crystallises in colourless needles melting at  $180^\circ$ , and is identical with the product described by Zatti and Ferratini (*loc. cit.*) as melting at  $172^\circ$ . When treated with potash and distilled in a current of steam, an oily *base*,



the hydroxide of the substituted ammonium, distils; the *aurochloride*,  $\text{C}_{15}\text{H}_{19}\text{N}\cdot\text{AuCl}_4$ , crystallises in yellow scales melting at  $142\text{--}145^\circ$ , and the *picrate*,  $\text{C}_{15}\text{H}_{22}\text{NO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , forms golden scales melting at  $121\text{--}122^\circ$ .

On decomposing the methiodide,  $\text{C}_{15}\text{H}_{22}\text{NI}$ , with potash in the cold, a *hydroxide*,  $\text{C}_{15}\text{H}_{22}\text{N}\cdot\text{OH}$ , separates, which crystallises from alcohol in large prisms melting at  $73\text{--}74^\circ$ ; the *aurichloride*,  $\text{C}_{15}\text{H}_{22}\text{N}\cdot\text{AuCl}_4$ , crystallises in leaflets melting at  $164\text{--}165^\circ$ , and the *picrate*,  $\text{C}_{15}\text{H}_{22}\text{NO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , forms yellow scales melting at  $129\text{--}130^\circ$ . The solid base is converted into its liquid isomeride by distillation in a current of steam, and the same change gradually occurs spontaneously.  
W. J. P.

**Constitution of Hydroquinolines from Indoles.** By ANTONIO PICCININI (*Gazzetta*, 1898, 28, ii, 51—67).—On crystallising Ferratini's so-called secondary dimethyltetrahydroquinoline (*Abstr.*, 1893, i, 602),  $\text{C}_{11}\text{H}_{15}\text{N}$ , with tartaric acid, it yields the *tartrate* of the *lævo*-component in large, colourless prisms melting at  $85\text{--}86^\circ$ ; the *hydrochloride*,  $\text{C}_{11}\text{H}_{15}\text{N}\cdot\text{HCl}$ , of the *lævo*-base melts at  $203\text{--}204^\circ$ , whilst that of the racemic base melts at  $198\text{--}199^\circ$ , and has the specific rotation  $[\alpha]_D = -15\cdot6^\circ$  in aqueous solution. The base, therefore, has the constitution  $\text{C}_6\text{H}_4\langle\text{CMe}_2\text{NH}\rangle\text{CHMe}$ , and is an indole derivative.

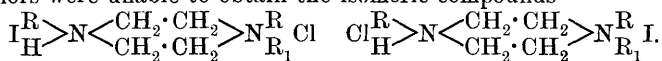
On oxidising tetramethyldihydroquinoline with alkaline perman-

ganate in the cold, and extracting with ether, a mixture of the trimethylindolinone,  $C_6H_4 \langle \begin{smallmatrix} CMe_2 \\ NMe \end{smallmatrix} \rangle CO$  (Brunner, Abstr., 1896, i, 625), and a compound of the composition  $C_{24}H_{30}N_2O_2$ , is obtained; the latter is a neutral substance which crystallises in colourless prisms melting at  $124^\circ$ , and its molecular weight was determined in freezing benzene. The so-called trimethyldihydroquinoline, therefore, has the constitution  $C_6H_4 \langle \begin{smallmatrix} CMe_2 \\ NMe \end{smallmatrix} \rangle C:CH_2$ .

Pentamethyldihydroquinoline,  $C_{14}H_{19}N$ , when oxidised with alkaline permanganate, yields the same trimethylindolinone, and has, therefore, the constitution  $C_6H_4 \langle \begin{smallmatrix} CMe_2 \\ NMe \end{smallmatrix} \rangle C:CM_e_2$ .

On distilling  $\alpha$ -methyldihydroindole hydrochloride with zinc dust, methylketol and quinoline are obtained, so that the formation of quinoline derivatives, on similarly treating Ferratini's secondary dimethyltetrahydroquinoline, does not prove the latter to contain a quinoline nucleus. W. J. P.

**Stereoisomerism in Piperazine and Ethylenediamine Derivatives.** By WILLEM VAN RIJN (*Chem. Centr.*, 1898, i, 380—381; from *Ned. Tijdsch. Pharm.*, 10, 5—16).—Attempts to obtain stereoisomerides depending on the presence of two asymmetric nitrogen atoms in the cases of derivatives of piperazine and methylethylpropylethylenediamine failed. Piperazonium bases containing four alkyl groups of the hexahydroterephthalic acid type cannot be prepared, as only one nitrogen atom is capable of combining with an alkylic haloid, and although the compounds thus formed can unite with an acid, the authors were unable to obtain the isomeric compounds



*Dibenzylpiperazine*,  $CH_2Ph \cdot N \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle N \cdot CH_2Ph$ , is prepared by heating molecular proportions of ethylene bromide and benzylamine, or, better, by the action of benzylic chloride on piperazine; it crystallises from alcohol in needles, melts at  $91$ — $92^\circ$ , is insoluble in water, soluble in ether, alcohol, chloroform, benzene, light petroleum, and carbon bisulphide. The *chloride* crystallises in plates, is slightly soluble in water, and gives precipitates with potassium dichromate, potassium ferrocyanide, auric chloride, and platonic chloride. The nitrate crystallises in leaflets and melts at  $155^\circ$ ; the bromide crystallises in small needles, and the sulphate is very easily soluble. The author also prepared diphenyldibenzylethylenediamine by the action of benzylic chloride and concentrated potassium hydroxide solution on diphenylethylenediamine; it crystallises from benzene in colourless crystals and melts at  $134$ — $135^\circ$ ; a nitroso-derivative could not be obtained.

The compounds of dibenzylpiperidine with one molecule of an alkylic haloid are easily prepared by warming a mixture of the components on the water-bath. *Dibenzylpiperazine methiodide* crystallises from alcohol in small prisms and melts at  $217^\circ$ . *Dibenzylpiperidine ethiodide* crystallises from hot water in white needles, melts at  $197^\circ$ , is

soluble in alcohol, methylic alcohol, chloroform, and carbon bisulphide, and very slightly soluble in ether, acetone, light petroleum, and benzene. *Dibenzylpiperazine propiodide* forms yellow needles, decomposes at  $260^{\circ}$ , and is slightly soluble in alcohol. *Dibenzylpiperidine isobutobromide* crystallises from hot water in colourless crystals, melts at  $195-196^{\circ}$ , is soluble in alcohol, chloroform, and acetone, and insoluble in carbon bisulphide, ether, benzene, and light petroleum. E. W. W.

**Isorosindones.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, 31, 2477—2482. Compare Abstr., 1898, i, 334).—Phosphorus pentachloride converts the alkylisosindones into unstable dichlorides which lose alkyl chloride when heated, yielding chloronaphthaphenazines (compare Abstr., 1898, i, 383).

*Chlorethyl-naphthaphenazonium chloride*,  $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{EtCl} \end{smallmatrix} \text{C}_{10}\text{H}_6$ , prepared by heating ethylisosindone with phosphorus oxychloride and phosphorus pentachloride on the water-bath, crystallises from alcohol in brownish aggregates; it dissolves readily in water, and the alcoholic solution has a feeble, greenish-brown fluorescence. The *platinochloride*, *aurichloride*, and *nitrate* crystallise in needles, and the *mercurichloride* in leaflets. *Chlorophenonaphthazine*,

$\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}_{10}\text{H}_6$ , obtained by heating the foregoing phenazonium chloride at  $170-180^{\circ}$ , crystallises from benzene in yellow needles; it melts at  $191^{\circ}$ , and the solution in concentrated sulphuric acid is cherry red.

*Methylisosindone*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_3\text{N} \\ | \\ \text{NMe} \cdot \text{C}_{10}\text{H}_{16} \end{smallmatrix}$ , is produced on heating an alcoholic solution of a methyl- $\beta$ -naphthylamine salt with nitrosophenol and an acid; it separates from a mixture of benzene and petroleum in black crystals having a metallic reflex, and melts at  $212-214^{\circ}$ . The *hydrochloride*, *hydrobromide*, and *hydriodide* are dissociated by hot water.

*Benzylisosindone*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_3=\text{N} \\ | \\ \text{N}(\text{CH}_2\text{Ph}) \end{smallmatrix} \text{C}_{10}\text{H}_6$ , prepared from benzyl- $\beta$ -naphthylamine and nitrosophenol, crystallises in brownish-violet needles and melts at  $210^{\circ}$ ; the solution in concentrated sulphuric acid is bluish-violet. The *hydrochloride*, *hydrobromide*, and *hydriodide* are crystalline.

*$\beta$ -Naphthylisosindone*, prepared from  $\beta$ -dinaphthylamine and nitrosophenol, separates from pyridine in black crystals having a metallic reflex; the solution in concentrated sulphuric acid is deep bluish-violet. The *hydrochloride*, *hydrobromide*, and *hydriodide* are crystalline. M. O. F.

**Hydroxyrosindines.** By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1898, 31, 2482—2485. Compare Abstr., 1895, i, 611).—Symmetrical hydroxyrosindone,  $\text{O} \begin{smallmatrix} \text{C}_{10}\text{H}_5\text{N} \\ | \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_3\text{OH}$ , otherwise called naphthasafranol, was first obtained from  $\text{B}_2$ -amidophenylrosinduline (Abstr., 1893, i, 335), and the methylic ether has been recently

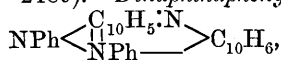


prepared from isorosindone methiodide by the action of alcoholic potash (Abstr., 1898, i, 338); although naphthasafranol is regenerated when this compound is heated with concentrated hydrochloric acid, methylic iodide converts it into a methylic ether which differs from the one which has been already described. Examination has shown this substance to be identical with the methoxyisorosindone described as melting at 274° (Abstr., 1897, i, 171).

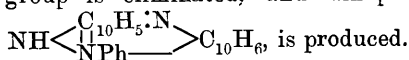
Naphthasafranol *methylic ether* crystallises from pyridine in slender, deep red prisms or needles, and melts at 308°; the solution in concentrated acid is reddish-violet. The *ethylic ether* melts at 269°.

M. O. F.

**Synthesis of Indulines.** By OTTO FISCHER and EDUARD HEPP (Ber., 1898, 31, 2485—2489).—*Dinaphthaphenylsafranine*,



formerly prepared from  $\alpha$ -amidoazonaphthalene hydrochloride, or from aniline and benzeneazo- $\alpha$ -dinaphthylamine, is readily obtained by heating nitrosophenyl- $\alpha$ -naphthylamine hydrochloride and phenyl- $\beta$ -naphthylamine with glacial acetic acid on the water-bath; it crystallises from boiling pyridine in bulky, dull gold needles, and melts at 268°. When the hydrochloride is heated with aqueous ammonia (1 mol.) and alcoholic ammonia (15—20 mols.), one phenylic group is eliminated, and dinaphthaposafranine (naphthinduline),

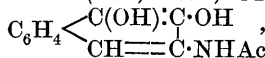


*Ethylidinaphthaphenylaposafranine*,  $\text{NPh} \left\langle \begin{array}{c} \text{C}_{10}\text{H}_5\text{:N} \\ | \\ \text{NEt} \end{array} \right\rangle \text{C}_{10}\text{H}_6$ , obtained from nitrosophenyl- $\alpha$ -naphthylamine hydrochloride and ethyl- $\beta$ -naphthylamine, crystallises from pyridine in black prisms having a metallic reflex, and melts at 254—255°. A mixture of glacial acetic and concentrated hydrochloric acids at 210°, eliminates aniline, and gives

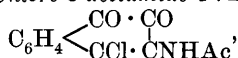
rise to *ethylidinaphthaposafranine*,  $\text{O} \left\langle \begin{array}{c} \text{C}_{10}\text{H}_5\text{:N} \\ | \\ \text{NEt} \end{array} \right\rangle \text{C}_{10}\text{H}_6$ , which crystallises from alcohol in golden needles, and melts at 247°; the *hydrochloride* forms greenish prisms, and the *nitrate* crystallises from alcohol in red needles.

M. O. F.

**3-Acetamido- $\beta$ -naphthaquinone and some of its Derivatives.** By FRIEDRICH KEHRMANN and FRITZ ZIMMERLI (Ber., 1898, 31, 2405—2412).—3-Acetamidonaphthaquinol,

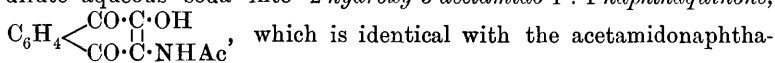


which is formed when the triacetyl derivative is heated with the calculated amount of dilute aqueous soda, decomposes at about 170°. The corresponding *quinone*, obtained by the action of chromic acid mixture on the solution of the quinol, crystallises in dark brownish-red needles, which melt at 214—216° and form a dark blood-red solution in alcohol. 4-Chloro-3-acetamido-1:2-naphthaquinone,



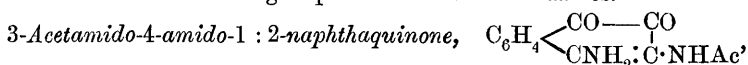
is prepared by treating the foregoing compound with hydrochloric acid, and oxidising the quinol which is formed by chromic acid mixture. It forms well developed, garnet-red prisms, which melt and decompose at about  $170^{\circ}$ , and reacts readily with orthophenylenediamine hydrochloride to form 6-chloro-5-acetamidonaphthaphenazine,  $C_6H_4 \begin{smallmatrix} <N:C \cdot C_6H_4- \\ N:C \cdot C(NHAc) \end{smallmatrix} > CCl$ , which crystallises in pale yellow needles and melts at  $292^{\circ}$ .

4-Chloro-3-acetamido-1:2-naphthaquinone is readily converted by dilute aqueous soda into 2-hydroxy-3-acetamido-1:4-naphthaquinone,



linic acid described by Kehrmann and Weichardt (Abstr., 1889, 1197). This compound is probably formed by intramolecular change from the hydroxy-1:2-naphthaquinone, which is doubtless the first product.

3-Acetamido-1:2-naphthaquinone is converted by ammonia and monamines into substances which are at the same time orthodiamines and quinones, and are therefore capable of yielding substances which contain the characteristic groups of imidazoles and azines.

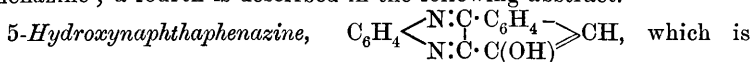


formed by the action of ammonia on acetamidonaphthaquinone, crystallises in chocolate-coloured needles melting at  $222^{\circ}$ .

3-Acetamido-4-methylamido-1:2-naphthaquinone is obtained by the action of methylamine on the acetamidoquinone, and forms dark reddish-brown crystals melting at  $245-246^{\circ}$ ; it is converted by aqueous soda into acetamidohydroxy-1:4-naphthaquinone. The foregoing compound reacts with orthophenylenediamine to form dimethylimidazonenaphthaphenazine,  $C_6H_4 \begin{smallmatrix} <N:C-C-N \\ N:C \cdot C_6H_4 \cdot C \cdot NMe \end{smallmatrix} > CMe$ , which crystallises in orange-coloured needles melting at  $264^{\circ}$ . The monacid salts are not dissociated by water.

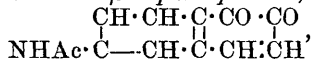
3-Acetamido-4-anilido-1:2-naphthaquinone forms dark brown, glistening crystals melting at about  $308^{\circ}$ . When the solution in acetic acid is boiled, it is converted into phenylmethyl-3:4-imidazolone-1:2-naphthaquinone,  $CO \begin{smallmatrix} <CO-C-N \\ C_6H_4 \cdot C \cdot NPh \end{smallmatrix} > CMe$ , which crystallises in light, garnet-red needles, and melts at  $305-306^{\circ}$ .

3-Acetamidonaphthaquinone reacts with orthophenylenediamine to form 5-acetamidonaphthophenazine,  $C_6H_4 \begin{smallmatrix} <N:C \cdot C_6H_4- \\ N:C \cdot C(NHAc) \end{smallmatrix} > CH$ , which crystallises in pale yellow needles melting at  $240^{\circ}$ , and is not fluorescent. Hydrochloric acid converts it into the 5-amidonaphthaphenazine hydrochloride which crystallises in small, almost colourless needles. The free amido-compound forms short, blood-red prisms melting at  $198-199^{\circ}$ . This compound is the third isomeride of amidonaphthaphenazine; a fourth is described in the following abstract.

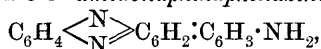


formed when the amido-compound is heated with 5 per cent. sulphuric acid at 140—150°, crystallises in lemon-yellow needles melting at 199°. A. H.

**3'-Acetamido- $\beta$ -naphthaquinone and some of its Derivatives.** By FRIEDRICH KEHRMANN and M. MATIS (*Ber.*, 1898, 31, 2413—2418. Compare the foregoing abstract).—1:3-Dinitro- $\beta$ -naphthol is converted by reduction and treatment of the product with acetic anhydride into triacetyldiamido- $\beta$ -naphthol, and this is partially hydrolysed by dilute aqueous soda, yielding *diacetamido- $\beta$ -naphthol*,  $C_{14}H_{14}N_2O_3$ , which crystallises in almost colourless needles melting at 235°. On oxidation with chromic acid mixture, the naphthol is converted into 3'-*acetamido- $\beta$ -naphthaquinone*,



which forms dark red, granular crystals, and decomposes at 180°. This substance is much more closely allied to  $\beta$ -naphthaquinone both in appearance and chemical behaviour than is the isomeric compound previously described. With orthophenylenediamine hydrochloride, it yields 3''-*acetamidonaphthaphenazine*,  $C_{18}H_{13}N_3O$ , which crystallises in long, pale yellow needles melting at 274°; on treatment with sulphuric acid, it is converted into 3''-*amidonaphthaphenazine*,



which crystallises in orange-coloured, lustrous plates melting at 217°. Aniline converts the quinone into 4-*anilido-3-acetamido- $\beta$ -naphthaquinone*,  $NHAc \cdot C_6H_3 < \begin{array}{c} \text{CO} - \text{CO} \\ | \quad | \\ \text{C}(\text{NHPh}) : \text{CH} \end{array}$ , which is a red, crystalline powder

almost insoluble in alcohol and melting and decomposing at 282°. 3'-*Acetamido- $\beta$ -naphthaquinonemonoxime*, crystallises in pale yellow needles which decompose at 230°. A dioxime could not be prepared. 3'-*Amido- $\beta$ -naphthaquinonemonoxime* is precipitated in red needles when the alkali solution of the acetyloxime is boiled and acidified with acetic acid, but these soon change into yellow crystals. When these are redissolved in alkali and again precipitated by acid, the red needles are again produced. It crystallises from alcohol in orange-coloured plates which decompose at 190°. These two modifications of the oxime correspond in their properties with those of the oxime of 4-amido- $\beta$ -naphthaquinone. The isomerism may possibly be due to the presence of a nitroso-group in one form and an isonitroso-group in the other. A. H.

**Azonium Compounds from Benzil. III.** By FRIEDRICH KEHRMANN and C. NATCHEFF (*Ber.*, 1898, 31, 2425—2428. Compare Abstr., 1891, 945).—The *nitrate* of the azonium compound formed from benzil and orthamidodiphenylamine crystallises in sulphur yellow needles, has a bitter taste, and melts at 172°.

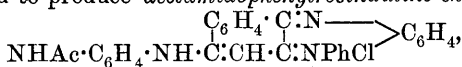
The compound from benzil and diamidodiphenylamine yields a *chloride*,  $C_{26}H_{20}N_3Cl$ , which forms lustrous, ruby-red crystals. The *acetyl* derivative,  $C_{28}H_{22}N_3OCl$ , crystallises in golden-yellow needles.

Orthamidodiphenylamine yields, with nitrobenzil, a base,  $C_{26}H_{19}N_3O_3$ ,

which crystallises in orange-yellow needles melting at  $169^{\circ}$ , and can also be obtained as a brick-red, flocculent precipitate. The *ferrichloride*,  $C_{26}H_{18}N_3O_2FeCl_4$ , forms readily soluble, yellow crystals. Benzil condenses with nitrophenylorthophenylenediamine to form a compound,  $C_{26}H_{19}N_3O_3$ , which separates in lemon-yellow, crystalline granules, and melts at  $161^{\circ}$ ; an intermediate compound,  $CPhO \cdot CPh \cdot N \cdot C_6H_3(NO_2) \cdot NHPh$ , is first formed which has no basic properties and crystallises in long, pale yellow needles melting at about  $200^{\circ}$ .

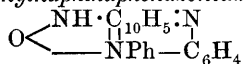
The authors have recently obtained experimental evidence that these compounds are not true azonium bases, and this will form the subject of a future communication. A. H.

**The Azonium Compounds prepared from  $\beta$ -Naphthoquinone-4-sulphonic Acid and Phenylorthophenylenediamine.** By FRIEDRICH KEHRMANN and C. LOCHER (*Ber.*, 1898, 31, 2428—2437. Compare *Abstr.*, 1896, i, 700).—The sulphonic acids of both phenylnaphthaphenazonium and phenylisonaphthaphenazonium exist in the form of anhydrides, the elements of water having been eliminated from the azonium hydroxyl and the sulphonic group. Phenylnaphthaphenazonium-6-sulphonic acid readily reacts with alkalis, amines, hydroxylamine, and benzenesulphinic acid, the sulphonic group being in all cases eliminated. Caustic soda converts it into rosindone, whilst ammonia produces rosinduline; methylamine acts in a similar manner to ammonia, and converts the acid into methylrosinduline, the *nitrate* of which crystallises in red, lustrous plates, which are almost insoluble in cold water and decompose at about  $257^{\circ}$ , whilst the *aurichloride* forms small, garnet red, insoluble needles. Aniline also behaves in a similar manner, yielding phenylrosinduline. Acetylparaphenylenediamine reacts with the sulphonic acid to produce *acetamidophenylosinduline chloride*,

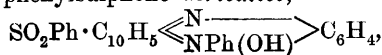


which crystallises in greyish-brown needles having a metallic lustre. When this salt is decomposed by sodium carbonate, the anhydride of the free *base* is formed,  $C_{30}H_{22}N_4O$ , and separates in brown crystals. On heating the substance with 50 per cent. sulphuric acid, it is converted into *amidophenylosinduline sulphate*,  $C_6H_4 < \overset{\overset{NH}{\parallel}}{N} \cdot \overset{\overset{C_{10}H_5 \cdot N}{\parallel}}{C} \cdot NH_2 \cdot SO_4 \cdot NPh - C_6H_4$ ;

the corresponding *chloride* crystallises in bluish-violet needles with a metallic lustre and forms a *platinochloride*,  $(C_{28}H_{22}N_4)_2 \cdot PtCl_6$ , which is a dark violet, crystalline precipitate, and is quite insoluble in water. Hydroxylamine converts the sulphonic acid into a compound which is probably 6-oxamidophenylnaphthaphenazonium anhydride,



This substance crystallises in small, ruby-red prisms, and decomposes at  $233^{\circ}$ ; it is insoluble in alkalis, and is not attacked by acetic anhydride. Benzenesulphinic acid also reacts with the sulphonic acid, forming a phenylsulphone derivative,



which resembles rosindone in physical properties, but cannot have a paraquinoid constitution, so that its existence is a strong argument in favour of Nietzki's orthoquinoid formula. It forms hard, reddish-brown crystals, and melts at  $287^{\circ}$ .

Phenylisonaphthaphenazonium-9-sulphonic acid reacts with amines in a manner different from its isomeride, violet or blue sulphonic acids of the isorosindulines being obtained; 2-dimethylamidophenyl-isonaphthaphenazonium-4'-sulphonic anhydride,  $\text{O} \begin{array}{c} \text{NPh} \\ | \\ \text{SO}_2 \cdot \text{C}_{10}\text{H}_5 \cdot \text{N} \end{array} \text{C}_6\text{H}_3 \cdot \text{NMe}_2$ , is formed by the action of dimethylamine on the isosulphonic acid, and crystallises in small, dark violet needles which have a coppery lustre.

The mother liquors of the two azonium-sulphonic acids, to which reference has already been made, contain a compound which crystallises in long, dark violet needles melting at  $212^{\circ}$ ; this is probably

2'-hydroxyrosindone,  $\text{O} \begin{array}{c} \text{NPh} \\ | \\ \text{C}_{10}\text{H}_4(\text{OH}) \cdot \text{N} \end{array} \text{C}_6\text{H}_4$ , although its constitution cannot be considered as definitely ascertained. A. H.

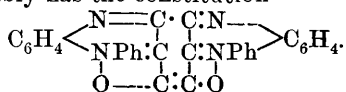
**Action of Alkylorthodiamines on Tetrahydroxyquinone and Rhodizonic Acid.** By FRIEDRICH KEHRMANN and ALBERT DURET (*Ber.*, 1898, 31, 2437—2442).—Tetrahydroxyquinone readily undergoes condensation with phenylorthophenylenediamine hydrochloride

to form 1:2:4-trihydroxyphenylaposafranone,  $\text{O} \begin{array}{c} \text{NPh} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4(\text{OH})_3 \end{array} \text{N}$ ,

which crystallises in brownish-green, dichroic needles with a steel-blue lustre; the triacetate crystallises in reddish-violet needles, and decomposes at  $220$ — $225^{\circ}$ . The trihydroxy-compound dissolves in aqueous alkalis with a red coloration, which soon becomes yellow, and acids then precipitate 2-hydroxyphenylaposafranonequinone,  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$ , crystallising in tablets which have a dark green, metallic lustre and decompose at about  $275^{\circ}$ . It has not yet been ascertained whether this substance is a para- or an ortho-quinone. Dilute nitric acid converts the trihydroxy-compound into a substance,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_4$ , which crystallises in pale yellow, microscopic needles, and is readily soluble in aqueous soda; its constitution has not been determined.

1:2:4-Trihydroxymethylaposafranone,  $\text{O} \begin{array}{c} \text{NMe} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4(\text{OH})_3 \end{array} \text{N}$ , obtained by the condensation of tetrahydroxyquinone with methylorthophenylenediamine, crystallises in green plates which have a faint metallic lustre, and decompose at  $250$ — $255^{\circ}$ .

Rhodizonic acid undergoes a complicated reaction with phenylorthophenylenediamine, yielding trihydroxyaposafranone, along with a compound,  $\text{C}_{30}\text{H}_{18}\text{N}_4\text{O}_2$ , which forms crystalline granules having a violet, metallic lustre, and yielding a crystalline hydrochloride; this substance seems to be formed from 1 mol. of rhodizonic acid and 2 of the base, and probably has the constitution



A. H.

**An Isomeride of Diphenylfluorindine.** By FRIEDRICH KEHRMANN and ALBERT DURET (*Ber.*, 1898, 31, 2442—2444. Compare Abstr., 1896, i, 631).—The chloride of isodiphenylfluorindine yields a base which contains no oxygen, and probably has the constitution  $C_6H_4 \left\langle \begin{smallmatrix} NPh \\ \text{---} N \end{smallmatrix} \right\rangle C_6H_2 \left\langle \begin{smallmatrix} N \\ \text{---} NPh \end{smallmatrix} \right\rangle C_6H_4$ , so that it is isomeric with diphenylfluorindine. On adding ammonia to the chloride, it is precipitated in grass-green, microscopic crystals. The *ferrichloride*,  $C_{30}H_{22}N_4Cl_2 \cdot FeCl_3$ , crystallises in dark blue tablets, and the *platinochloride* is an indigo-blue, crystalline precipitate which is insoluble in water. The *dichromate* is also an insoluble crystalline precipitate, whilst the *aureichloride* is a flocculent powder. A. H.

**Hydroxytriazolecarboxylic Acid and Hydroxytriazole.** By WILHELM MANCHOT (*Ber.*, 1898, 31, 2444—2447).—3-Hydroxytriazole-

5-carboxylic acid,  $\begin{smallmatrix} C(OH) \cdot N \\ | \\ N \text{---} NH \end{smallmatrix} \rangle C \cdot COOH$ , prepared by heating diazotriazolecarboxylic acid with 12—15 times its weight of dilute sulphuric or nitric acid until the evolution of nitrogen is at an end, is sparingly soluble in cold water or alcohol, but dissolves readily in the hot liquids; it crystallises from water in small, apiculate, prismatic needles frequently aggregated to rosettes. It contains  $1H_2O$ , which is driven off with difficulty at  $120^\circ$ ; it then melts and decomposes at  $205^\circ$ . It is a fairly strong acid, and, with silver nitrate, its aqueous solution yields a white, and, with copper sulphate, a bluish-green precipitate.

3-Hydroxytriazole, which is easily prepared from the foregoing acid by heating it at its melting point, agrees in properties with the compound prepared by Widman and Cleve (*Abstr.*, 1898, i, 335); it gives a red coloration when mixed with an alkaline solution of diazobenzenesulphonic acid, thus exhibiting a phenolic character, and supplying further evidence of the aromatic nature of the triazole nucleus.

If the decomposition of the above diazo-compounds has been effected by means of nitric acid, the mother liquors, on evaporation, leave a residue which gives a yellow precipitate with silver nitrate, and forms a red solution with alkalis.

The author makes a preliminary announcement of the fact that, whilst reduction of diazotriazolecarboxylic acid to the corresponding hydrazine is difficult to accomplish, he has succeeded in obtaining a satisfactory yield of benzyltriazylhydrazone (m. p. =  $225^\circ$ ). A. L.

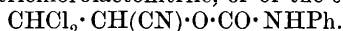
**Diketones of Tetrahydro- $\beta$ -oxazole derived from the Phenylurethanes of some Hydroxy-acids.** By EUGENE LAMBLING (*Compt. rend.*, 1898, 127, 188—190).—It has been previously shown (this vol., i, 52) that the action of phenylcarbimide on compounds of the type  $COOR \cdot CHR \cdot OH$  gives rise to phenylurethanes of the formula  $COOR \cdot CHR \cdot O \cdot CO \cdot NHPh$ , from which the corresponding acids may be obtained by successive treatment with alkali and acid. When boiled with water, these acids yield anhydrides of the constitution

$CO \left\langle \begin{smallmatrix} CHR \cdot O \\ NPh \cdot CO \end{smallmatrix} \right\rangle$ , which may be regarded as diketo-derivatives of tetra-

hydro- $\beta$ -oxazole. The following derivatives were thus obtained from the phenylurethanes of lactic, trichlorolactic, glycollic, phenylglycollic, and  $\alpha$ -hydroxyisobutyric acids.

The diketone,  $\text{CO} \begin{smallmatrix} \text{CHMe} \cdot \text{O} \\ \text{NPh} - \text{CO} \end{smallmatrix}$ , crystallises in microscopic needles melting at  $141^\circ$ , and is slightly soluble in cold, and more soluble in boiling, water, soluble in alcohol and ether. It is insoluble in a cold concentrated solution of sodium carbonate, but, on warming, the sodium salt of the phenylurethane of lactic acid is regenerated. This diketone has also been prepared by Travers, who obtained from it an acid to which he ascribed the constitution  $\text{OH} \cdot \text{CHMe} \cdot \text{CO} \cdot \text{NPh} \cdot \text{COOH}$ , a formula which is not in accordance with the reactions studied by the author.

The diketone,  $\text{CO} \begin{smallmatrix} \text{CH}(\text{CHCl}_2) \\ \text{NPh} - \text{CO} \end{smallmatrix} \text{O}$ , crystallises from boiling alcohol in slender needles melting at  $202^\circ$ . It may be prepared by the general method indicated above, and also by the hydrolysis of the phenylurethane of trichlorolactonitrile, or of the compound



The latter is obtained by the action of aqueous soda on trichlorolactonitrile phenylurethane, and crystallises in microscopic needles melting at  $150^\circ$ . In this reaction, dichloroacetanilide,  $\text{CHCl}_2 \cdot \text{CO} \cdot \text{NHPH}$ , crystallising in needles melting at  $116^\circ$ , is also produced.

The diketones,  $\text{CO} \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{NPh} - \text{CO} \end{smallmatrix}$ ,  $\text{CO} \begin{smallmatrix} \text{CHPh} \cdot \text{O} \\ \text{NPh} - \text{CO} \end{smallmatrix}$ , and  $\text{CO} \begin{smallmatrix} \text{CMe}_2 \cdot \text{O} \\ \text{NPh} - \text{CO} \end{smallmatrix}$ , are crystalline compounds melting at  $121^\circ$ ,  $122^\circ$ , and  $118$ – $119^\circ$  respectively, and, when boiled with concentrated sodium carbonate solution, yield the phenylurethanes from which they are derived.

Experiments made with the phenylurethanes derived from ethylic  $\beta$ -hydroxybutyrate and from methylic salicylate, which might be expected to yield closed chain compounds of six elements, have hitherto yielded no definite result.

N. L.

**Benzisothiazole.** By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, 31, 2185–2187).—When benzisothiazole,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ | \\ \text{N} - \text{S} \end{smallmatrix}$

(*Abstr.*, 1895, i, 432; 1896, i, 215), is heated with phenylhydrazine, ammonia, hydrogen sulphide, and benzene are evolved, and orthamidobenzaldehydephenylhydrazone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{NHPH}$  (Eliasberg and Friedländer, *Abstr.*, 1892, 1106), is formed. When it is heated with hydrazine hydrate, ammonium sulphide is evolved, and orthamidobenzylideneazone,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH})_2\text{N}_2$ , is obtained; this can also be prepared by heating a solution of orthamidobenzaldehyde with hydrazine hydrate; it is a yellow, crystalline substance, which melts and decomposes at about  $244^\circ$  and has feebly basic properties; the yellow hydrochloride, with  $1\text{HCl}$ , was prepared and analysed.

C. F. B.

**New Creatinine Derivative.** By WILLIAM KRAMM (*Chem. Centr.*, 1898, i, 37–38; *from Centr. med. Wiss.*, 35, 785–787).—By treating

urine with sodium nitroprusside and sodium hydroxide solution and, as soon as the colour changes to yellow, adding acetic acid and shaking vigorously, a crystalline precipitate of *nitrosocreatinine*,  $C_4H_6N_4O_2$ , is obtained. It is soluble in dilute mineral acids, in dilute sodium hydroxide solution, and in excess of ammonia; it is precipitated from its yellow alkaline solutions by acetic acid or carbonic anhydride, and gives a silver compound which is insoluble in water. Nitrosocreatinine may also be prepared from a solution of pure creatinine.

E. W. W.

**Allocaffeine.** By HENRY A. TORREY (*Ber.*, 1898, 31, 2159—2162).—Allocaffeine,  $C_8H_9N_3O_5$ , prepared from tetramethyluric acid (E. Fischer, *Abstr.*, 1898, 1, 180) was boiled with plenty of water; carbonic anhydride was evolved, and the allocaffeine went into solution. The product, *allocaffuric acid*,  $C_7H_{11}N_3O_4$ , left on evaporating the water, was crystallised from ethylic acetate; the crystals, when they first separated, melted at  $158^\circ$ , but after remaining for several days in contact with the mother liquor, they melted at  $164$ — $165^\circ$ . When warmed with baryta water for a few minutes at  $40^\circ$ , the acid is decomposed into dimethylcarbamide and a *monomethylamide* of *mesoxalic acid*; this substance, which has acid properties and forms an insoluble barium salt, was only obtained as a syrup, but its *phenylhydrazone*,  $C_{10}H_{11}N_3O_3$ , which melts and decomposes at about  $158^\circ$ , was obtained in yellow crystals and analysed; when it is heated with 30 per cent. caustic soda, a sodium salt separates at first, but on heating to  $100^\circ$  a new product,  $C_9H_{11}N_3O$ , melting at  $205$ — $209^\circ$  is obtained. If allocaffuric acid is boiled with baryta water, the products are dimethylcarbamide, methylamine, and mesoxalic acid. C. F. B.

**Tetrahydropapaverine.** By GUIDO GOLDSCHMIEDT (*Monatsh.*, 1898, 19, 321—332. Compare *Abstr.*, 1888, 611).—Pope and Peachey (*Trans.*, 1898, 893) have been able to decompose *r*-tetrahydropapaverine into its two optically active constituents by the aid of  $\delta$ -bromocamphor-sulphonic acid; the author had attempted the same resolution by the aid of tartaric acid, but without success. Even when an excess of tartaric acid is employed, the sparingly soluble normal tartrate,  $(C_{20}H_{25}NO_4)_2C_4H_6O_6 + 17H_2O$ , and not the acid tartrate, crystallises out. When dried at  $105^\circ$ , the salt still retains  $1H_2O$ , which it loses when heated at  $155^\circ$ .

When the base is crystallised from water or from very dilute alcohol, or when it is obtained by precipitating an aqueous solution of the hydrochloride with ammonia, it forms small, anhydrous needles, but when crystallised from dilute methylic alcohol, large prisms,  $(C_{20}H_{25}NO_4)_2 + CH_3O$ , are obtained, which lose their alcohol of crystallisation if heated or when left exposed to the air; when crystallised from absolute methylic alcohol, however, crystals without alcohol of crystallisation are obtained.

*Tetrahydropapaverine nitrosamine*, obtained by adding an excess of potassium nitrite to a solution of tetrahydropapaverine hydrochloride, crystallises from alcohol in well-developed, amber-coloured pyramids melting at  $180$ — $182^\circ$ ; it dissolves readily in acetone, chloroform,



benzene, ethylic acetate, and warm alcohol, is only sparingly soluble in ether, and insoluble in light petroleum. When warmed with alcohol and hydrochloric acid, tetrahydropapaverine hydrochloride is obtained.

*Tetrahydropapaveroline hydriodide*,  $C_{16}H_{17}NO_4 \cdot HI$ , obtained when tetrahydropapaverine is heated for 4 hours with hydriodic acid (sp. gr. = 1.27) and red phosphorus, crystallises in long, satiny needles containing  $1\frac{1}{2}H_2O$ . The *hydrochloride*, obtained by shaking an aqueous solution of the hydriodide with freshly precipitated silver chloride, crystallises with  $2H_2O$ .

*Tetrahydropapaveroline* is best obtained by dissolving the hydrochloride in water free from air, and decomposing with the requisite quantity of sodium hydrogen carbonate dissolved in water saturated with carbonic anhydride; it forms a slightly violet coloured, micro-crystalline precipitate which is readily coloured by air or alkalis, is sparingly soluble in the usual organic solvents, turns brown at  $200^\circ$ , and melts and decomposes at about  $255^\circ$ . Aqueous solutions of the hydrochloride reduce Fehling's solution on boiling, and when treated with potassium and ammonium hydroxides turn violet. With ferric chloride, it gives the same reaction as catechol. J. J. S.

**Derivatives of Cinchona Alkaloids.** By WILHELM KOENIGS and MAX HÖPPNER (*Ber.*, 1898, 31, 2355—2364. Compare Abstr., 1896, i, 264 and 328).—Deoxycinchonidine, mixed with methylic alcohol and methylic iodide and allowed to remain in darkness at ordinary temperatures for 24 hours, gives rise to a colourless, crystalline *methiodide*,  $C_{19}H_{22}N_2 \cdot MeI$ , which melts at  $167$ — $168^\circ$ . When treated with alkalis, this compound undergoes the same change which Claus (Abstr., 1881, 289) has previously observed in the case of other alkylic haloids of cinchona bases.

When the methiodide, dissolved in very dilute sulphuric acid, is mixed with excess of caustic soda solution, and allowed to remain at ordinary temperatures, it is gradually transformed into *methyldeoxycinchonidine*, which crystallises from ether in colourless, feathery needles arranged in fan-like clusters, and melts at  $64$ — $65^\circ$ . It is readily soluble in alcohol, ether, and benzene, and sparingly in light petroleum. A 10 per cent. alcoholic solution is feebly dextrorotatory, and a solution in dilute sulphuric acid has a blue fluorescence. The *mercurichloride* crystallises from dilute alcohol in needles, and the corresponding cadmium and zinc compounds are crystalline and more soluble than those of deoxycinchonidine. The *platinochloride*,  $C_{20}H_{24}N_2 \cdot H_2PtCl_6$ , separates in reddish-yellow crystals, and blackens at  $200^\circ$  without melting.

When methyldeoxycinchonidine is heated with 20 per cent. aqueous phosphoric acid, it yields lepidine, but no base like apocinenine is obtained on continued heating with concentrated hydrobromic acid. Oxidation of a cold solution of the base with permanganate in dilute sulphuric acid solution gives rise to chinchonic and *n*-methylcincholeuonic acids.

Further methylation of methyldeoxycinchonidine results in the formation of a *methiodide*,  $C_{20}H_{24}N_2 \cdot MeI$ , which crystallises from methylic

alcohol or water in white prisms and decomposes at  $251^{\circ}$ . The methiodide does not appear to yield a dimethyl base on treatment with alkalis.

*Deoxycinchonine methiodide*,  $C_{19}H_{22}N_2, MeI$ , prepared in a similar manner to deoxycinchonidine methiodide, crystallises from water in thick, colourless, tetragonal tablets and melts at  $176^{\circ}$ . On treatment with caustic soda, it yields a base which, like methyldeoxycinchonidine, melts at  $64^{\circ}$  and yields the above methiodide melting at  $251^{\circ}$ . Methyldeoxycinchonine and methyldeoxycinchonidine seem, therefore, to be identical. The deoxy-bases of quinine, conchicine, cinchonidine, and cinchonine are far more poisonous towards animals and infusoria than the corresponding parent substances.

When the hydrogen iodide additive product of cinchonine is heated for some time with aqueous phosphoric acid, a trace of formaldehyde is given off, and two bases which do not contain iodine are obtained. The one produced in larger quantity has properties resembling those of Lippmann and Fleissners' allocinchonine and also those of Hesse's apoisocinchonine; like the latter, it melts at  $216^{\circ}$ , whilst its sulphate and dihydriodide resemble those of the former; the platinochloride,  $C_{19}H_{22}N_2O, H_2PtCl_6$ , crystallises with  $2H_2O$ .

Cinchenine (cinchine), when heated on the water bath with excess of concentrated sulphuric acid, yields a crystalline sulpho-derivative insoluble in alkalis, to which the name of *sulphocinchine* [sulphocinchenine] is given, and which has the composition  $C_{19}H_{20}N_2SO_3$ ; it crystallises from ethylic or methylic alcohol in colourless prisms, turns yellow at  $150^{\circ}$ , becomes red at  $200^{\circ}$ , decomposes at  $280^{\circ}$ , and is insoluble in water, ethylic acetate, and ether but dissolves readily in dilute acids, chloroform, and benzene.

Sulphocinchenine, when warmed for some time with dilute sulphuric acid or alcohol, is converted into an isomeride *cinchinesulphonic* [*cincheninesulphonic*] acid which is readily soluble in alkalis.

Chromic acid oxidises sulphocinchenine to cinchonic acid and a sulphonic acid the barium salt of which is soluble in water and alcohol; when heated with phosphoric acid at  $170$ — $180^{\circ}$ , the base yields lepidine and an uncrystallisable sulphonic acid.

Dihydrocinchenine, which always accompanies cinchenine when the latter is prepared from commercial cinchonine, is not attacked by the sulphuric acid in the above reaction; it appears likely that the vinyl group, to which the  $SO_3$  attaches itself in the case of cinchenine, is in dihydrocinchenine hydrogenised to an ethyl group. G. T. M.

**Salts of Hydrazoic Acid with some Organic Bases.** By HERBERT POMMERHNE (*Arch. Pharm.*, 1898, 236, 479—486).—The hydrazoic acid employed was prepared by Dennstedt and Göhlich's (*Chem. Zeit.*, 1897, 21) method.

*Strychnine hydrazoate*,  $C_{21}H_{22}N_2O_2, N_3H + H_2O$ , prepared by dissolving the alkaloid in the acid, separates in beautiful, silken needles which, on exposure to air, lose a large portion of the acid, and this takes place completely on heating at  $100^{\circ}$ . The amount of hydrazoic acid in the salt was therefore estimated by titration with N/10 sodium hydroxide.

*Brucine hydrazoate*,  $C_{23}H_{26}N_2O_4, N_3H + 3H_2O$ , is a crystalline substance with similar properties; *quinine hydrazoate* crystallises in hard,

glistening, anhydrous plates; *codeine hydrazoate* crystallises in bunches of silken needles containing  $2\text{H}_2\text{O}$ . None of these salts explodes on drying.

Morphine does not form a salt with hydrazoic acid, nor do nicotine, coniine, pyridine, piperidine, quinoline, or tetrahydroquinoline.

A. W. C.

**Periodides of Certain Alkaloids, and the Volumetric Estimation of Alkaloids as Higher Periodides.** By ALBERT B. PRESCOTT and HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1898, 20, 706—728).—On adding iodine dissolved in aqueous potassium iodide to a solution of a salt of an alkaloid, keeping the latter in excess throughout, the lowest periodide (generally a tri-iodide) is precipitated; if, however, the solution of the alkaloid is gradually added to the iodine solution, the highest periodide is generally formed exclusively. The periodides described below were all prepared as follows; a solution of the alkaloid (1 gram) in 200 c.c. of water acidified with hydrochloric or sulphuric acid, was gradually added to 500 c.c. of water containing 1 per cent. of free iodine and  $1\frac{1}{2}$  per cent. of potassium iodide; after shaking until the solution became clear, the product was collected, and, when possible, recrystallised.

*Atropine enneaiodide*,  $\text{C}_{17}\text{H}_{23}\text{NO}_3\cdot\text{HI}\cdot\text{I}_8$ , prepared in this way, is a dark brown, almost black, powder, which dissolves only sparingly in ether, chloroform, benzene, or carbon bisulphide, but readily in hot alcohol; it separates from the latter unchanged in dark green prisms or leaflets, but is decomposed by hot water and by a concentrated solution of potassium iodide. When heated, it loses iodine at  $90^\circ$ , and melts at  $140^\circ$ . The additive iodine in the salt, and in those following, was determined by dissolving it in alcohol, adding an excess of standard sodium thiosulphate, and estimating the excess by means of standard iodine. The total iodine was determined by boiling the periodide suspended in water with zinc dust during 15 minutes, filtering, and estimating the iodine in solution, either gravimetrically or volumetrically, by means of silver nitrate. Quantitative experiments show that the hydriodic acid present in atropine periodide owes its origin to double decomposition taking place between the hydrochloric acid originally combined with the base and the potassium iodide present in the iodine solution. The enneaiodide is, however, also formed on adding atropine (20 grams) to a warm solution of iodine (30 grams) in chloroform (500 c.c.), but in this case the origin of the hydriodic acid is doubtful; if carbon bisulphide or tetrachloride is employed instead of chloroform, no periodide is formed.

On warming an alcoholic solution of atropine enneaiodide, or, better, atropine itself with the theoretical quantity of iodine, and an excess of mercury until the colour of the iodine is discharged, *monatropine hydriodide mercuric iodide*,  $\text{C}_{17}\text{H}_{23}\text{NO}_3\cdot\text{HI}\cdot\text{HgI}_2$ , separates in lustrous, yellow crystals, which melt at  $80\text{--}90^\circ$ , are sparingly soluble in ether and chloroform, but very soluble in warm alcohol. On treating an alcoholic solution of this compound with an excess of potassium iodide, the salt,  $(\text{C}_{17}\text{H}_{23}\text{NO}_3)_2\cdot 2\text{HI}\cdot\text{HgI}_2$ , is formed; the latter crystallises in white, silky needles, melts at  $98\text{--}99^\circ$ , and is easily soluble in warm alcohol and water.

*Strychnine heptiodide*,  $C_{21}H_{22}N_2O_2, HI, I_6$ , is a dark brown powder which cannot be recrystallised, as it easily decomposes into iodine, and the tri-iodide; *brucine heptiodide*,  $C_{23}H_{26}N_2O_4, HI, I_6$ , closely resembles it. The tetriodide,  $C_{17}H_{19}NO_3, HI, I_3$ , described by Jörgensen (*J. pr. Chem.*, 1870, [ii], 2, 437), is the only periodide obtainable from morphine. *Aconitine heptiodide*,  $C_{33}H_{45}NO_{12}, HI, I_6$  (?), was prepared by adding aconitine to an excess of iodine dissolved in potassium iodide solution; *aconitine tri-iodide*,  $C_{33}H_{45}NO_{12}, HI, I_3$  (?), prepared by adding a 1 per cent. solution of iodine to an acidified solution of aconitine, separates from alcohol in beautiful, brown-red crystals, melts at  $211-212^\circ$ , and is sparingly soluble in ether, benzene, and chloroform.

The total iodine present in the periodides of brucine, morphine, and aconitine cannot be determined by the method given above; the following has to be adopted. The periodide is left in contact during 30 minutes with zinc dust and concentrated aqueous ammonia, the latter expelled by heating, water added, and the mixture boiled during 10 minutes; the liquid is filtered into a separating funnel, the residue of zinc washed with hot water until the solution has a volume of 200—300 c.c., and, when cold, the latter is rendered slightly acid with very dilute sulphuric acid. Twenty c.c. of carbon bisulphide and 10—12 drops of concentrated sulphuric acid saturated with nitrous acid are added, the iodine dissolved in the carbon bisulphide, transferred to a wetted filter, and the residue again extracted with carbon bisulphide. The iodine is washed on the filter, first with water, then with very dilute sodium hydrogen carbonate, and is transferred to a flask together with a 0.5 per cent. solution of the latter. Finally, the iodine is titrated with standard sodium thiosulphate.

The alkaloids dealt with can be determined volumetrically as follows. An acidified solution of the base is initially diluted by trial so that on adding 10—15 c.c. of it to 25—30 c.c. of decinormal iodine solution, making up to a known volume, and well shaking, the clear liquid obtained has a very dark red colour; the iodine present in an aliquot portion of the latter is then determined. From the amount of iodine required to precipitate as periodide a known volume of the solution of the alkaloid, the concentration of the latter is determined by using the following factors, which give the ratio of alkaloid to iodine used in its precipitation: atropine, 0.2849; strychnine, 0.4390; brucine, 0.5179; morphine, 0.74918; and caffeine, 0.3834. The factors were verified in the first four cases by direct experiment.

*Volumetric assay of opium.*—One gram of finely powdered opium is triturated with 2—3 c.c. of a mixture containing 5 c.c. of concentrated aqueous ammonia, 5 c.c. of alcohol, 20 c.c. of ether, and 10 c.c. of chloroform, and the vessel covered and left during 3 hours; 15 grams of finely powdered common salt is carefully mixed with the mass, the vessel left open during 3 hours at  $30-35^\circ$ , and subsequently exposed in a vacuum over solid paraffin until perfectly dry. The product is then extracted with benzene in a percolator, until, on evaporating a drop or two of the extract, dissolving in 4—5 drops of acidified water, and adding a solution of iodine in potassium iodide, no precipitate is obtained. The removal of alkaloids other than morphine is thus effected, and the morphine is extracted in the same

way by means of acetone (about 200 c.c.). After removing the latter by evaporation at a temperature not exceeding  $40^{\circ}$ , the residue is rubbed up with fresh lime-water, and the liquid, without filtering, is diluted to 100 c.c. After being vigorously shaken in a stoppered bottle during 30 minutes, the solution is filtered until exactly 50 c.c. has passed through, the filtrate is slightly acidified with hydrochloric acid, and 25 c.c. of decinormal iodine slowly added, keeping the vessel gently shaken. Water is added to a convenient volume, and the mixture shaken vigorously during about 20 minutes until, on standing, a perfectly clear, dark red liquid is obtained. Half the total volume is filtered, and the excess of iodine determined by the usual method. One gram of iodine = 0.74918 gram of morphine. W. A. D.

**The Hyoscine-scopolamine Question.** By LOUIS MERCK (*J. Soc. Chem. Ind.*, 1897, 16, 515—516. Compare Schmidt, Abstr., 1897, i, 385).—E. Merck's "hyoscine," obtained from *Hyoscyamus*, consists entirely of scopolamine; although very large quantities of solanaceous roots have been investigated in the Merck laboratories, no alkaloid,  $C_{17}H_{23}NO_3$ , corresponding with Ladenburg's hyoscine, could be obtained. Gadamer has, however, isolated a base, *ψ-hyoscyamine*,  $C_{17}H_{23}NO_3$ , from *Duboisia myoporoides*, which melts at  $132\text{--}134^{\circ}$  and is isomeric with atropine and hyoscyamine. The only other alkaloids present in *Duboisia myoporoides* are hyoscyamine, scopolamine, and considerable quantities of amorphous bases. Although it is often stated that hyoscine (that is, scopolamine) is present in the residual bases obtained in the manufacture of atropine, the investigation of large quantities of these has led the author to conclude that the statement is incorrect; the scopolamine found by others is probably to be attributed to the roots used being imperfectly sorted. In discussing the identity of Hesse's atroscine with Schmidt's "inactive scopolamine," it is pointed out that, whereas the scopolamine hydrobromide obtained from *Hyoscyamus* always possesses normal rotatory power ( $[\alpha]_D = -24\text{--}25^{\circ}$ ), that obtained from *Scopolia* roots shows a much lower optical activity ( $[\alpha]_D = -13.47^{\circ}$ ). Since the conditions as regards alkali were identical in the two preparations, the author concludes that two chemically identical scopolamines which differ in optical activity, exist ready formed in *Scopolia*, whilst one only is present in *Hyoscyamus*. W. A. D.

**Identity of Hesse's Atroscine and E. Schmidt's *i*-Scopolamine.** By JOHANNES GADAMER (*Arch. Pharm.*, 1898, 236, 382—392).—The author has definitely proved that atroscine (Hesse) and *i*-scopolamine (Schmidt) are the same alkaloid. Both can be prepared from scopolamine hydrobromide ( $[\alpha]_D = -13^{\circ} 31'$ ) by rendering alkaline with sodium carbonate and extracting with a mixture of chloroform and ether. If, after evaporation, the residue be rubbed with water and alcohol and then cooled, crystals of atroscine (Hesse) melting at  $37\text{--}38^{\circ}$  separate, but if a crystal of *i*-scopolamine (Schmidt) be added to the residue, compact, transparent crystals of the latter alkaloid melting at  $56\text{--}56.5^{\circ}$  are formed. Both substances are hydrates of the same alkaloid: atroscine contains  $2H_2O$  and is the labile form, whilst scopolamine contains  $1H_2O$  and is the stable form.

When a few drops of concentrated sodium hydroxide are added to scopolamine hydrobromide, the alkaloid is decomposed and sodium atropate is formed; more dilute caustic soda does not produce decomposition.

If atrosine (Hesse) is dissolved in alcohol, water added until a milkiness appears, and then a crystal of scopolamine, the latter alkaloid separates; and, conversely, atrosine can be converted into scopolamine when the amount of the labile form is three times as great as the dissolved stable form, and also when a freshly prepared solution of anhydrous *i*-scopolamine (Schmidt) is sown with a crystal of atrosine (Hesse).

The aurichlorides obtained from both alkaloids are identical, and melt at the same temperature, 208°. A. W. C.

**Bebeerine and Buxine.** By MAX SCHOLTZ (*Arch. Pharm.* 1898, 236, 530—541. Compare Abstr., 1896, i, 710).—The first part of the paper deals with some experiments which have already been noticed in this Journal (*loc. cit.*). Herzig and Meyer (Abstr., 1898, i, 53) have shown that bebeerine, both crystalline and amorphous, contains one methoxyl group and one methyl group attached to a nitrogen atom, and therefore the formula of the alkaloid is  $\text{OH} \cdot \text{C}_{16}\text{H}_{14}\text{O}(\text{OMe}) \cdot \text{NMe}$ .

When bebeerine is distilled with zinc dust, it yields orthocresol and methylamine; potassium permanganate and chromic acid decompose it completely; nitric acid gives rise to a yellow, amorphous powder, probably containing nitro-groups, which does not melt at 300°; potassium ferricyanide replaces two hydrogen atoms by one oxygen atom yielding the substance  $\text{C}_{18}\text{H}_{19}\text{NO}_4$ , which, after crystallisation from alcohol, decomposes without melting at 260°, and hydrogen peroxide produces a yellow mass partially soluble in glacial acetic acid. The soluble portion is an acid,  $\text{C}_{18}\text{H}_{17}\text{NO}_7$ , melting at 270°, and the insoluble portion an aldehyde,  $\text{C}_{18}\text{H}_{17}\text{NO}_6$ , crystallising in colourless needles and melting at 255°; its phenylhydrazone separates from alcohol in yellow needles melting at 166°.

*Dibebeerine-xyleneammonium bromide*,  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NBr} \cdot \text{C}_{18}\text{H}_{21}\text{O})_2$ , prepared by the action of orthoxylylenic bromide on the crystalline base dissolved in chloroform, forms colourless leaflets melting at 258°. It follows, therefore, that the nitrogen atom is not united to an aromatic residue, because aromatic tertiary amines do not combine with xylylenic bromide (Abstr., 1898, i, 565).

The author has been unable to crystallise buxine from methylic alcohol, and therefore considers that this alkaloid may not be identical with bebeerine (compare Flückiger, *Neues Jahrbuch der Pharm.*, 31, 257). A. W. C.

**Alkaloids contained in *Lycoris radiata* Herb.** By K. MORISHIMA (*Chem. Centr.*, 1898, i, 254—255; from *Arch. exp. Path. Pharm.*, 40, 221—240).—From the alcoholic extract of the bulbs of *Lycoris radiata* Herb. (*Nerine japonica* Mig.) the author has isolated lycorine and sekisanine. *Lycorine*,  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_8$ , crystallises in large, colourless polyhedra, becomes yellow at 235°, and decomposes at 250°, is very slightly soluble in water, ether, alcohol, and chloroform, and easily so in acids. Its solutions give the reactions of alkaloids. In concen-

trated sulphuric acid, it forms a colourless solution which rapidly becomes yellowish-red, and in concentrated nitric acid a brownish-yellow solution; with sodium molybdate and concentrated sulphuric acid, it gives a dirty green which turns blue, and with potassium permanganate and concentrated sulphuric acid a yellow coloration which passes through violet to yellow again. The *platinochloride* melts at  $210^{\circ}$  and the *hydrochloride*,  $C_{32}H_{32}N_2O_8 \cdot 2HCl + 2H_2O$ , crystallises in slender needles and melts at  $208^{\circ}$ . *Sekisanine*,  $C_{34}H_{36}N_2O_9$ , obtained from the alcoholic mother liquor of lycorine by means of ether, crystallises from dilute alcohol in long, colourless, four-sided prisms, melts at about  $200^{\circ}$ , is very slightly soluble in water, ether, chloroform and benzene, rather easily in alcohol, and easily in acids; the solutions in concentrated sulphuric and nitric acids are yellow. It is precipitated by all the common reagents for alkaloids. With sodium molybdate and concentrated sulphuric acid, it gives a yellow, and with potassium permanganate and concentrated sulphuric acid a reddish, coloration, which turns violet and then yellow. The platinum salt melts at  $194^{\circ}$ .

Pharmacologically, lycorine belongs to the emetine group, acting as an emetic, then causing diarrhoea followed by paralysis. E. W. W.

**Hydrolysis of the Pectin of Gentian Root.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 8, 49—52).—When the pectin extracted from gentian root by water at  $110^{\circ}$  (Abstr., 1898, i, 607) is oxidised by dilute nitric acid (sp. gr. = 1.15), mucic acid is obtained. When heated with 3 per cent. sulphuric acid for  $1\frac{1}{2}$  hours at  $110^{\circ}$ , the pectin is hydrolysed, arabinose being formed; the latter was identified by its melting point, crystalline form, and specific rotatory power. No other sugar could be detected. W. A. D.

**Action of Soluble Ferments on the Pectic Products of Gentian Root.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 8, 145—150).—The soluble ferments produced during the growth of *Aspergillus niger* partially hydrolyse the pectose of gentian root, converting it into pectin. They have, however, no action on pectin prepared from gentian by digesting the latter with water at  $110^{\circ}$  (Abstr., 1898, i, 607). Although pectin obtained in this way is not changed by saliva or by emulsin, it is converted into a substance possessing cupric-reducing power by diastase precipitated from malt extract by alcohol. From this, the author concludes that malt-diastase consists of at least three enzymes; an *amylase*, capable of hydrolysing starch, a *trehalase* which hydrolyses trehalose, and an enzyme which effects hydrolysis of the pectin of gentian root. W. A. D.

**Presence in Malt of a Soluble Ferment Acting on Pectin.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1898, 127, 191—194. Compare preceding abstracts).—Powdered gentian root was extracted with boiling 80 per cent. alcohol and then heated with water at  $110^{\circ}$  in an autoclave. The solution of pectin thus obtained is readily acted on by diastase at the ordinary temperature, the action being much facilitated by the addition of a little chalk, which serves the

purpose of neutralising the slight acidity of the pectin. After 48 hours, the liquid is found to have acquired reducing properties and is no longer coagulated by pectase, whilst the addition of two volumes of 95 per cent. alcohol only produces a small, pulverulent precipitate. Neither the amylase of saliva nor the ferments (trehalase, &c.) of *Aspergillus* have any action on pectin, and hence it is inferred that the diastase of malt contains a special ferment, other than amylase or trehalase, capable of acting on the pectin of gentian. N. L.

**Proteolytic Enzyme of Yeast Extract.** By L. GERET and MARTIN HAHN. (*Ber.*, 1898, 31, 2335—2344. Compare Abstr., 1898, ii, 245 and 246).—This enzyme is not only capable of decomposing the albumin present in the yeast extract, but also attacks additional quantities of albumin from other sources. When 20 c.c. of a solution of egg-albumin, containing 3.5 per cent. of coagulable albumin, is allowed to digest for 6 days with 20 c.c. of yeast extract containing 5.2 per cent. of albumin, it is found that, not only is the whole of the latter rendered soluble, but also 21 per cent. of the added albumin. If a sample of yeast extract be coagulated after one hour's digestion, the filtrate is found to contain leucine and tyrosine, and traces of albumoses, but no peptone.

Yeast extract to which 2 per cent. of peptone or albumose is added, gives at first a marked biuret reaction, but after digestion for 3 days this is no longer obtained. The total nitrogen in the digested extract is determined, and the amount present in organic bases is obtained by precipitating these with phosphotungstic acid, the difference giving the amount present in the form of amido-acids. A table is given showing the change in these quantities after definite intervals of time; as the digestion is prolonged, the amount of basic nitrogen reaches a maximum and then decreases, so that after two weeks the ratio of basic to amido-acidic nitrogen is the same as at the commencement of the experiment.

When air is passed through yeast extract for a given time, it is found that the amount of coagulated albumin is less than when hydrogen is passed through it.

The amount of hypoxanthine precipitable by ammoniacal silver solution without previous boiling with dilute sulphuric acid increases with the time of digestion. Agitation of the yeast extract, either by shaking in a vacuum or by passing air or hydrogen through the mixture, favours the formation of this precipitable hypoxanthine. There is still in the extract a further quantity of hypoxanthine which is only precipitated by ammoniacal silver after boiling with dilute sulphuric acid. The amount of this "latent form" of hypoxanthine is not altered by mechanical agitation.

The amount of phosphorus as phosphoric acid in the extract is determined in the usual way after removing the albumin by mercuric chloride and hydrochloric acid; it is found to increase with the time of digestion. After 1 hour, two-thirds of the total phosphorus is present as phosphoric acid, and after 9 days one-fifth still remains combined with organic compounds. The total quantity of sulphur is inconsiderable; and only a small proportion of this is converted into



sulphuric acid; the amount separating in this form increases slightly with the time.

The activity of the proteolytic enzyme of yeast is diminished, but not destroyed, by 1 per cent. hydrocyanic acid, and it recovers its original strength if the acid be again removed.

Tables are also given indicating the presence of proteolytic enzymes in extracts from *Sarcina rosea* and tuberculosis and typhus bacilli.

The formation of these enzymes in animal and vegetable cells appears to be more common than is generally supposed; it remains to be decided whether the enzyme is excreted by the individual cell or whether it is retained in the cell-contents and only rendered manifest when the cell undergoes disruption. G. T. M.

**Taka-diastrase.** By WINTHROP E. STONE and H. E. WRIGHT (*J. Amer. Chem. Soc.*, 1898, 20, 639—647).—The authors have compared the action of taka-diastrase on potato starch with that of diastrase precipitated from malt extract by alcohol. The iodine test for starch shows that the latter is acted on more rapidly, at the outset, by taka-diastrase than by malt-diastrase; in the former case, an almost immediate change from the typical blue of the starch-iodine compound to reddish and violet tints takes place, whereas in the latter a longer time elapses before this occurs. The complete conversion, however, of starch into forms which no longer give colour reactions with iodine is effected much more rapidly by malt-diastrase than by taka-diastrase. The specific rotatory powers of the conversion products of starch by malt- and taka-diastrase indicate that, under the same conditions, the latter effects a more rapid transformation to maltose than the former, and this result was confirmed by determining in each case the actual amount of maltose formed.

Owing to the incomplete conversion of starch into maltose by taka-diastrase, the latter cannot be used as a substitute for malt-diastrase in determining starch in vegetable materials; thus a sample of wheat which was found to contain 55.46 per cent. of starch by using malt extract, appeared to contain only 52.94 per cent. when taka-diastrase was employed. W. A. D.

**A Product of the Decomposition of Albumin.** By JACQUES M. ALBAHARY (*Compt. rend.*, 1898, 127, 121—124).—When dry egg-albumin is mixed with water and amorphous phosphorus, and iodine is gradually added, a reaction takes place with development of heat, and after some time a white precipitate separates on the surface of a yellow liquid. This precipitate contains no iodine and leaves no ash when burnt; it consists solely of carbon, hydrogen, nitrogen, oxygen, and sulphur. When dried at 110°, it becomes reddish-brown, hard, brittle, and transparent, melts and decomposes at 260—270°, is almost insoluble in water and solutions of normal alkali carbonates, and also in solutions of sodium phosphate or sodium chloride. It dissolves, however, in presence of alkali hydroxides, especially ammonia, and is reprecipitated by dilute acids, but dissolves in strong organic acids. With sodium hydroxide, it yields a salt which crystallises from aqueous alcohol in long needles, and begins to decompose at 250° but does not melt at 270°. It also forms, in presence of hydrochloric acid, a picrate,

a gold salt, and a platinum salt, the first two being readily crystallisable. The molecular weight of the gold salt is 2011 and of the nitrogen compound 1670. The author calls the compound *ovalbuminic acid*; it contains C, 50.05; H, 7.04; N, 17.20; S, 2.14; O, 23.54.

When a solution of the sodium salt is dialysed, it yields an almost neutral liquid in which calcium salts produce a white precipitate and which is coagulated by a mixture of sodium chloride with calcium or magnesium sulphate, although sodium chloride alone has no effect.

The acid gives the xanthoproteic, biuret, Molisch, Millon and Adamkiewicz reactions, and is reprecipitated from its hydrochloric acid solution by phosphomolybdic and phosphotungstic acids and by Bouchardat's reagent. Its acetic acid solution gives, with potassium ferrocyanide, a greenish precipitate, which, when heated with a trace of hydrochloric acid, becomes deep blue. Its hydrochloric acid solution gives a blue coloration only with the ferrocyanide. C. H. B.

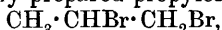
**Products of the Trypsin Fermentation of Casein.** By FRANZ RÖHMANN (*Ber.*, 1898, 31, 2188. Compare Abstr., 1898, i, 56).—By warming the crude leucine (*loc. cit.*) with phenylthiocarbimide, potassium hydroxide, and a little dilute alcohol, the leucine can be separated in the form of the phenylthiohydantoic acid, which changes, when kept, into the phenylhydantoin,  $C_4H_9 \cdot CH \begin{smallmatrix} \swarrow CO \cdot NPh \\ \searrow NH \cdot CS \end{smallmatrix}$ , melting at 178° (Aschan, Abstr., 1883, 1107; 1884, 907).

C. F. B

## Organic Chemistry.

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**Action of Bromine on Propylic Bromide in presence of Aluminium Bromide.** By A. MOUNEYRAT (*Compt. rend.*, 1898, 127, 273—276).—The author has applied to propylic bromide the method already used in the case of ethylic bromide (this vol., i, 1). One hundred grams of the substance to be brominated was heated with 20 grams of aluminium bromide and the calculated quantity of bromine. In this way, he has readily prepared propylenic bromide,



from propylic bromide, and tribromopropane,  $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CHBr}_2$ , from the propylenic bromide. In the formation of the tribromopropane, which is accompanied by small quantities of its isomeride,  $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ , and a tetrabromopropane, it is probable that the propylene bromide loses hydrogen bromide, and is converted into bromopropylene, which at once combines with bromine, or possibly with hydrogen bromide.

*Tetrabromopropane*,  $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CHBr}_2$ , is obtained in a similar way from either of the derivatives  $\text{CH}_3 \cdot \text{CHBr} \cdot \text{CHBr}_2$ , or



and, in its turn, yields pentabromopropane,  $\text{CHBr}_2 \cdot \text{CHBr} \cdot \text{CHBr}_2$ .

C. H. B.

**Action of Acetylene on Mercuric Nitrate.** By KARL A. HOFMANN (*Ber.*, 1898, 31, 2783—2787. Compare *Abstr.*, 1898, i, 635).—H. Erdmann and Köthner (this vol., i, 21) describe a substance obtained by the action of acetylene on a hot solution of mercuric nitrate as a double compound of mercurous carbide and nitrate,  $\text{HgC}:\text{CHg}, \text{HgNO}_3 + \text{H}_2\text{O}$ . It is not an acetylide, however, for it gives no acetylene when heated with hydrochloric acid, but aldehyde instead. Neither is it a mercurous compound, for, when it is digested for  $\frac{1}{4}$  hour with dilute hydrochloric acid, 83·8 per cent. of mercuric chloride is formed, but only 2·3 per cent. of mercurous chloride, and this, no doubt, on account of the reducing action of the aldehyde simultaneously formed; further, potassium cyanide solution dissolves the compound without deposition of mercury, and ammonia produces no black coloration. The substance analysed by Erdmann and Köthner contained a little mercury; after removal of this by digestion with dilute nitric acid, the analytical numbers agree with the formula  $\text{NO}_3 \cdot \text{Hg} \cdot \text{C}(\text{Hg}_2 \cdot \text{O}) \cdot \text{CHO}$ , that of a substituted aldehyde.

The compound is best prepared by dissolving yellow mercuric oxide (20 grams) in dilute nitric acid (70 c.c. of 30 per cent. acid and 500 c.c. of water), filtering, and passing a fairly rapid current of acetylene for 2 hours through the solution at a temperature of 18°. The precipitate is then collected, digested three times with 8 per cent. nitric acid (150 c.c.) at the ordinary temperature for 6 hours, filtered, washed with alcohol and ether, and dried under diminished pressure over sulphuric acid.

C. F. B.

**Acetylene Tetrabromide and Tribromomethylene.** By KARL ELBS and J. NEWMANN (*J. pr. Chem.*, 1898, [ii], 58, 245—254).—In preparing acetylene tetrabromide from acetylene generated from calcium carbide, the gas is best purified from hydrogen phosphide by passing it through a solution of mercuric chloride acidified with hydrochloric acid. The pure tetrabromide is an almost colourless liquid boiling at 124—126° under a pressure of 15 mm. When reduced with zinc dust and acetic acid, or zinc dust and sodium ethoxide in alcoholic solution, the principal products are acetylene dibromide and tribromomethylene, and small amounts of ethylene dibromide. Aluminium amalgam reduces the tetrabromide so rapidly and completely to acetylene dibromide that it may be used as a means of preparing that substance.

Attempts to replace bromine in acetylene tetrabromide by iodine or acetyl groups proved unsuccessful; the action of aniline, dimethylaniline, or alcoholic ammonia causes the production of tribromomethylene.

When the tetrabromide is heated with bromine and aluminium in sealed tubes at 90—95°, hexabromethane is produced.

Bromine acts readily on tribromomethylene, producing pentabromethylene; iodine reacts but slightly, whilst chlorine gives rise to chlorotribromomethylene, crystallising in colourless needles melting at 35° (compare Denzel, *Abstr.*, 1880, 228), and uniting with bromine to form chloropentabromethane melting at 170°.

Zinc dust acts on tribromomethylene, producing acetylene; concentrated sulphuric acid gives rise to pentabromethane; fuming sulphuric acid decomposes the substance completely; and nitrous anhydride produces *tribromonitroethylene* as a heavy, pale yellow liquid, with penetrating odour, boiling at 108—110° at 21 mm. (compare Scholl and Brenneisen, *Abstr.*, 1898, i, 345).

Chlorine acts on pentabromethane at 200—205°, with production of chlorotribromomethylene, whilst antimony pentachloride gives rise to hexachlorethane.

A. W. C.

**Hydrocarbon, C<sub>3</sub>H<sub>4</sub>, a Secondary Product of the Decomposition of Barium Pyromucate.** By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 614—616).—The hydrocarbon, C<sub>3</sub>H<sub>4</sub>, obtained when barium pyromucate is distilled (see this vol., i, 120), has a somewhat aliacious odour, and precipitates an alcoholic solution of mercuric chloride, but not ammoniacal cuprous chloride or silver nitrate. When treated with bromine, it yields a small quantity of a *dibromide* boiling at about 50° under reduced pressure, but the chief product is a *tetrabromide*, C<sub>3</sub>H<sub>4</sub>Br<sub>4</sub>, a liquid boiling at 162° at 20 mm. pressure. This compound has not been obtained pure, as it is extremely hygroscopic, and as it is not identical with allylene tetrabromide, it is probable that the hydrocarbon has the constitution  $\text{CH}_2 \begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix}$ .

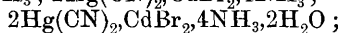
J. J. S.

**Action of Ammonia on Zinc and Mercuric Cyanides, and on Haloid Double Salts of the Latter.** By RAOUL VARET (*Ann. Chim. Phys.*, 1897, [vii], 10, 5—18. Compare *Abstr.*, 1896, i, 3, 633, ii, 88, 149, 512; 1897, i, 585, ii, 38, 99).—The compound

$\text{Zn}(\text{CN})_2, 2\text{NH}_3, \text{H}_2\text{O}$ , obtained in transparent, prismatic crystals is produced by the action of ammonia on aqueous solutions of zinc cyanide; the compound  $\text{Zn}(\text{CN})_2, 2\text{NH}_3$ , is formed in alcoholic ammoniacal solutions, or by the action of dry ammonia on the heated cyanide. Both these substances are very soluble in aqueous and alcoholic ammoniacal solutions, and rapidly decompose on exposure to the air.

The compound  $2\text{Hg}(\text{CN})_2, 4\text{NH}_3, \text{H}_2\text{O}$  separates in white, prismatic needles when a saturated solution of mercuric cyanide in concentrated ammonia is cooled in a freezing mixture; the compound  $2\text{Hg}(\text{CN})_2, 2\text{NH}_3, \text{H}_2\text{O}$  is obtained when a saturated solution of mercuric cyanide in less concentrated ammonia is allowed to crystallise at  $0^\circ$ ; both substances are very unstable, and are completely resolved into their constituents when heated to  $100^\circ$ . The compound  $\text{Hg}(\text{CN})_2, 2\text{NH}_3$  results from the employment of alcoholic solutions; it separates in transparent, prismatic needles, which decompose rapidly on exposure to air. The compound  $\text{Hg}(\text{CN})_2, \text{NH}_3$ , produced in an aqueous ammoniacal solution of mercuric cyanide in the presence of excess of the salt, separates from the filtrate in hard, granular crystals; it is more stable than the preceding compounds, but is completely decomposed on heating at  $100^\circ$ . No definite compound results from the action of dry, gaseous ammonia on warm mercuric cyanide. The double salt,  $\text{Hg}(\text{CN})_2, \text{HgCl}_2$ , when treated with alcoholic ammonia, is resolved into its components; mercuric chloride gives rise to an insoluble compound,  $2\text{HgCl}_2, 3\text{NH}_3$ , whilst mercuric cyanide yields the substance  $\text{Hg}(\text{CN})_2, 2\text{NH}_3$ . A greyish-white substance,  $2\text{Hg}_2(\text{CN})_2\text{Cl}_2, 3\text{NH}_3$ , is obtained by the action of dry ammonia on gently heated mercuric chlorocyanide. The chlorocyanide, when treated with aqueous ammonia, gives a precipitate of mercuric ammonium chloride,  $\text{NH}_2\text{HgCl}$ ; if zinc cyanide be added to the mixture, the precipitate redissolves, and on concentrating the solution the double salt,  $2\text{Hg}(\text{CN})_2, \text{ZnCl}_2, 4\text{NH}_3$ , is obtained in nodular crystals; this compound is also produced by the action of aqueous ammonia on the double salt,  $2\text{Hg}(\text{CN})_2, \text{ZnCl}_2, 7\text{H}_2\text{O}$ .

The latter method is employed in preparing the following series of analogously constituted double salts.  $2\text{Hg}(\text{CN})_2, \text{ZnBr}_2, 4\text{NH}_3$ ;  $2\text{Hg}(\text{CN})_2, \text{CuCl}_2, 4\text{NH}_3$ ;  $2\text{Hg}(\text{CN})_2, \text{CuBr}_2, 4\text{NH}_3$ ;



$2\text{Hg}(\text{CN})_2, \text{CdBr}_2, 4\text{NH}_3$ ;  $2\text{Hg}(\text{CN})_2, \text{CdI}_2, 4\text{NH}_3$ . These compounds are crystalline, and the copper and cadmium derivatives do not evolve ammonia when heated to  $100^\circ$ .

G. T. M.

**Action of Chlorine on Secondary Alcohols.** By ANDRÉ BROCHET (*Ann. Chim. Phys.*, 1897, [vii], 10, 134—144).—This paper gives a detailed account of the ultimate action of chlorine on isopropyl alcohol and methylhexylcarbinol; the results obtained have already been published (see *Abstr.*, 1895, i, 259; 1897, i, 4).

G. T. M.

**Action of Chlorine on Primary Alcohols.** By ANDRÉ BROCHET (*Ann. Chim. Phys.*, 1897, [vii], 10, 289—380).—This paper contains a very detailed account of work which has already been published. The theory of the chlorination of ethylic alcohol is fully discussed, and the work of previous investigators compared with the results

obtained by the author with other primary alcohols. The action of chlorine on methylic alcohol (Abstr., 1895, i, 637, and 1896, i, 276), on propylic alcohol (Abstr., 1896, i, 114), and on isobutylic alcohol (Abstr., 1892, 1292; 1894, i, 484; and 1897, i, 3, 4) has already been made known.

The author puts forward the following generalisation. When chlorine acts on any primary alcohol, except methylic alcohol, the first product of reaction is a dichloro-derivative,  $C_nH_{2n}Cl \cdot CHCl \cdot OH$ ; this either passes into a monochloraldehyde,  $C_nH_{2n}Cl \cdot COH$ , by loss of hydrogen chloride, or condenses with another molecule of alcohol to form an unsymmetrical dichloroxide,  $C_nH_{2n}Cl \cdot CHCl \cdot O \cdot CH_2 \cdot C_nH_{2n+1}$ . This statement has been verified in the case of ethylic, propylic, isobutylic, and isoamylic alcohols (Abstr., 1898, i, 549). In the case of methylic alcohol, the initial product is chloromethylic alcohol, which, by elimination of water, is converted into symmetrical dichloromethylic oxide.

G. T. M.

**Action of Chlorine on Tertiary Amylic Alcohol.** By ANDRÉ BROCHET (*Ann. Phys. Chim.*, 1897, [vii], 10, 381—387).—Chlorine has no action on cold dimethylethylcarbinol in diffused daylight, but at the boiling point of the alcohol, it is rapidly absorbed without evolution of gas. The products of the reaction are fractionated; the lowest fraction contains tertiary amylic chloride (2-methyl-2-chlorobutane),  $CMe_2Cl \cdot CH_2Me$ , and chloramylene (2-methyl-3-chlorobutene),  $CMe_2 \cdot CMeCl$ . This mixture is treated with bromine and subsequently steam distilled, when amylic chloride is obtained in the distillate and chloramylene dibromide remains in the residue.

The higher fractions contain some unattacked alcohol and higher chlorinated derivatives of isopentane (2-methylbutane), dichlorisopentane,  $CMe_2Cl \cdot CHMeCl$ , and *trichlorisopentane*, have been isolated. The latter boils at  $176^\circ$ , its sp. gr. =  $1.215$  at  $15^\circ/4^\circ$ , and its index of refraction  $n_D = 1.472$  at  $21^\circ$ .

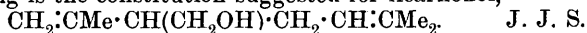
The chief product of the action of chlorine on the cold alcohol in the presence of sunlight is the above-mentioned dichlorisopentane. When the gas is passed into a boiling mixture of the alcohol and water, the chief product is trichlorisopentane; chloro-derivatives of higher boiling point, acetone, acetic, formic, and carbonic acids are also formed, but no amylic chloride could be detected. The first action of chlorine results in the formation of  $CMe_2Cl \cdot CHMeCl$ , this substance loses hydrogen chloride and forms  $CMe_2 \cdot CMeCl$ , addition of chlorine to the chloramylene produces  $CMe_2Cl \cdot CMeCl_2$ ; the amylic chloride is produced by a secondary reaction between the hydrochloric acid liberated and the unattacked alcohol.

G. T. M.

**Dextro-licarhodol.** By PHILIPPE BARBIER and GEORGES LÉSER (*Bull. Soc. Chim.*, 1897, [iii], 17, 590—596).—When pure licareol (boiling at  $86$ — $88^\circ$  under 10 mm. pressure) is heated with its own weight of acetic anhydride during 8 hours at  $150$ — $160^\circ$  and the product rectified under a pressure of 10 mm., three fractions are obtained. The first passes over between  $50^\circ$  and  $80^\circ$ , and consists mainly of terpenes; the second, passing over between  $80^\circ$  and  $105^\circ$ , consists mainly of unaltered licareol, and the third, boiling at  $105$ — $130^\circ$ , when further fractionated with the aid of a dephlegmator,

yields a colourless liquid boiling at 119—120° under 10 mm. pressure; this has the composition  $C_{10}H_{17} \cdot OAc$ . The higher fractions contain an ether,  $(C_{10}H_{17})_2O$ , boiling at 145—150° under 10 mm. pressure. The acetate is hydrolysed when the theoretical quantity of alcoholic potash is run in at the ordinary temperature, and the mixture then heated to 100° for an hour. The alcohol,  $C_{10}H_{18}O$ , licarhodol, thus obtained boils at 112—114° under 9 mm. pressure, has an agreeable odour, sp. gr. at 0° = 0.904, and rotatory power  $[\alpha]_D = +4.8'$ . The yield is about 800 grams from 5 kilos. of licareol. When oxidised with permanganate, licarhodol gives dimethyl ketone, terebic acid melting at 174°, and levulinic acid. When oxidised with chromic mixture, the products are methylheptenone,  $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot Ac$ , a small quantity of geranial-citral, and an acid,  $C_9H_{14}O_3$ , probably methylheptenonecarboxylic acid.

The following is the constitution suggested for licarhodol,



**Action of Neutral Salts on Glucose at a Higher Temperature.** By H. C. PRINSEN GEERLIGS (*Chem. Centr.*, 1898, i, 712; from *Arch. Suikerindustrie*, 1898).—The author finds that, not only do the salts of weak organic acids bring about the inversion of sugar in presence of glucose, but that at 100° they also act on the glucose, converting the dextrose into levulose, or when the latter is in excess, inversely converting it into dextrose; the same change is effected by the alkali salts of strong mineral acids (see following abstract), but to a very much smaller extent. The amount of change is proportional to the time during which the action has proceeded and to the concentration of the solution of the salt. A portion of the glucose is converted into organic acids, and it is these acids which sometimes interfere with Romijn's test for dextrose with iodine solution containing borax (*Arch. Suikerindustrie*, 1897, 1001) by absorbing iodine and forming iodoform. The feeble rotatory power of molasses containing much invert-sugar is due to the fact that the raw sugar molasses contain considerable quantities of salts of organic acids. E. W. W.

**Inversion of [Cane] Sugar by Neutral Salts in Presence of Glucose.** By H. C. PRINSEN GEERLIGS (*Chem. Centr.*, 1898, i, 711; from *Arch. Suikerindustrie*, 1898).—The quantity of sucrose inverted by neutral salts in presence of glucose (see *Arch. Suikerindustrie*, 1895) is approximately proportional to the time during which the action takes place and to the amount of glucose originally present; the quantity of salt (sodium chloride) has only a very slight influence on the action. The action of the glucose is due to the liberation of a very small quantity of acid by the formation of a glucosate of the base, but when calcium carbonate or a salt of a weak organic acid is added, the inversion is retarded or prevented. The more easily dissociated salts are the more active, thus magnesium chloride and the chlorides of the alkaline earths are more effective than the chlorides of the alkalis. The acids contained in the salts also have a great influence; the following salts of potassium are arranged in order of decreasing activity: chloride, bromide, nitrate, sulphate,

chlorate, oxalate, and succinate. Since the monosaccharides, dextrose, levulose, galactose, and lactose act like glucose, whilst the alcohols and the di- and tri-saccharides are inactive, the presence of an aldehyde group may be necessary to bring about the reaction.

E. W. W.

**Inversion of Saccharose by Water.** By BOHUSLAV RAÝMAN and OTTOKAR ŠULC (*Chem. Centr.*, 1898, i, 608—609; from *Zeit. Zuck.-Ind. Böhm.*, 22, 233—248. Compare Abstr., 1898, i, 348).—Saccharose is inverted by water at temperatures above 110°, but when acid is added the change takes place at a lower temperature. When extremely pure water is used, 10 per cent. and weaker solutions of saccharose are not affected by boiling for some hours, but when the water has a considerable conductivity, the action commences; generally speaking, the more concentrated the solution is after boiling, the more quickly inversion begins. When platinum vessels are used, the action occurs more rapidly, no matter how small the conductivity of the water, and in vessels of other metals inversion takes place with varying rapidity. The action of the metals of the platinum group in powder was investigated; of these, palladium induced the most rapid change, iridium alone retarded the action, and in many cases a faint acidity of the solution could be detected by Congo-red. When metallic vessels were used, this acidity was only apparent in the cases of copper and silver. The author ascribes the influence of metals partly to a hydrolytic action and partly to the formation of acids from the sugar; like acids, the metals are supposed to increase the chemical activity or "ionisation" of the water. The acid compounds are formed by a process of migration of the oxygen atoms analogous to certain reactions of sugars with alkalis and water. The oxidation of hydroxy-aldehydes and hydroxy-ketones is explained by a process of successive dehydration and hydration, whereby the groups  $\text{CH}_2\cdot\text{OH}$  and  $\text{CH}\cdot\text{OH}$  become  $\text{CH}_3$  and  $\text{CH}_2$  respectively, and the terminal carbon atoms either form carboxyl groups, formic acid, or carbonic anhydride. At the same temperature, increase of pressure diminishes the inversion effected.

E. W. W.

**Hydrolysis of Polysaccharides by Yeast Enzymes.** By ANUSCHAWAN KALANTHAR (*Zeit. physiol. Chem.*, 1898, 26, 88—101).—The author has studied the hydrolytic action of yeasts from various wines and beers, and from the Russian beverage "kissly-schtschi" and the Armenian beverage "mazun" on the polysaccharides. Pure cultures were prepared in each case, and both fresh and dried cells and aqueous extracts were employed. The polysaccharides experimented on were cane-sugar, maltose, lactose, melibiose, trehalose, melitriose (raffinose), melicitose, and  $\alpha$ -methylglucoside; 10 per cent. solutions were submitted to the action of the yeast, a little toluene being added to prevent alcoholic fermentation. The amount of monosaccharide produced was determined either by titration with Fehling's solution, or in the case of those polysaccharides which themselves reduce Fehling's solution, by ascertaining the amount of osazone produced with phenylhydrazine; the results



obtained are tabulated, and they indicate that the dried yeast and the aqueous extract possess a greater hydrolytic action than the fresh cells. Cane-sugar and raffinose were readily hydrolysed by all the forms of yeast employed. Maltose and  $\alpha$ -methylglucoside were usually decomposed to the same extent, but in one or two cases the latter compound appeared to be more readily attacked. Although melibiose and lactose are formed from the same components (*d*-glucose and *d*-galactose), they behave somewhat differently towards enzymes; the amount of the former hydrolysed varied with the temperature, only one wine yeast being capable of hydrolysing it at 25°, but in every case negative results were obtained with lactose.

Trehalose was hydrolysed by all the yeasts in the dried condition (compare Abstr., 1895, i, 441), except in the case of an orange-red yeast from "mazun"; fresh wine or distillery yeast also induced appreciable hydrolysis. Melicitose was hydrolysed by all the beer yeasts, with one exception.

The author adds a description of the preparation of "mazun" from milk. This beverage contains, besides bacilli and micrococci, nine species of yeast cells; seven of these have been isolated by Lindner and the author, and a table showing their hydrolytic action on maltose,  $\alpha$ -methylglucoside, trehalose, lactose, and cane-sugar is included in the paper.

G. T. M.

**Formation of Furfuraldehyde from Starch and its Derivatives.** By FAUSTO SESTINI (*L'Orosi*, 1898, 21, 109—113).—Furfuraldehyde, to which the odour of new bread is partly due, is produced by the simple heating of all varieties of bread, the crumb requiring to be heated to 140—160°, whilst for the crust, which has been already more strongly heated in the cooking, a temperature of 110—115° is sufficient. The aldehyde does not exist ready formed in the bread, since none is obtained from it by steam distillation, and its production must be attributed to the decomposition of pentoses derived from the bran, or to that of the starch and allied carbohydrates. Dry starch of various kinds was found to yield furfuraldehyde when heated to 180° and upwards, whilst if previously moistened with a minute quantity of sulphuric or hydrochloric acid, even a temperature of 100° was sufficient for its production. Nageli's "starch granulose," deprived of every trace of free acid, evolves furfuraldehyde at 100° or a few degrees higher, and the different varieties of dextrin behave in a similar manner. Furfuraldehyde may be obtained from pentoses without the aid of acids, as various kinds of gum were found to yield this substance when heated in the dry state to 180—200°, and also, if slightly moistened with water, at 120°. Two specimens of purified rice starch, when distilled with hydrochloric acid of sp. gr. = 1.06, yielded respectively 1.16 and 0.44 per cent. of furfuraldehyde, quantities far greater than could be derived from traces of pentoses possibly present in the starch and which, moreover, could not be detected therein. It follows from these results that the amount of furfuraldehyde obtainable from starch and allied carbohydrates is by no means a neglige-

able quantity, and this fact must be taken into account in estimating pentoses by the furfuraldehyde method. N. L.

**Derivatives of Bromethylamine and Bromopropylamine.** By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, 31, 2832—2839).—*Orthohydroxybenzylidenebromethylamine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_2\text{H}_4\text{Br}$ , formed by the condensation of bromethylamine hydrobromide with salicylaldehyde in presence of an alkali, crystallises in yellow needles, melting at  $56-57^\circ$ .

Ethylenepseudothiocarbamide is converted by nitrous acid into  $\mu$ -phenylthiazoline,  $\begin{array}{c} \text{CH}_2\cdot\text{S} \\ | \\ \text{CH}_2\cdot\text{N} \end{array} \gg \text{CPh}$ ; the picrate crystallises in lemon-yellow needles, which soften at  $165^\circ$  and melt at  $173-174^\circ$ , whilst the dichromate,  $(\text{C}_9\text{H}_9\text{NS})_2\cdot\text{H}_2\text{Cr}_2\text{O}_7$ , forms orange-yellow needles. The formation of this compound favours the supposition that ethylenepseudothiocarbamide contains an amido-group, and has the

constitution  $\begin{array}{c} \text{CH}_2\cdot\text{S} \\ | \\ \text{CH}_2\cdot\text{N} \end{array} \gg \text{C}\cdot\text{NH}_2$ . The thiazoline derivative is accompanied by a substance crystallising in flat, yellowish needles which melt and decompose at  $203-204^\circ$ . This compound is probably *nitroethylenepseudothiocarbamide*, but has not been obtained in sufficient quantity for further examination.

$\mu$ -Phenyl- $\beta$ -methylthiazoline,  $\begin{array}{c} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2-\text{N} \end{array} \gg \text{CPh}$ , is obtained from propylenepseudothiocarbamide, and is identical with that previously obtained from thiobenzamide (Gabriel and von Hirsch, *Abstr.*, 1897, i, 120). *Nitropropylenepseudothiocarbamide*,  $\text{C}_4\text{H}_7\text{NS}\cdot\text{NO}_2$ , crystallises in flat, oblique needles, which melt and decompose at  $166^\circ$ .

Mercaptothiazoline is decomposed by hydrochloric acid at  $155^\circ$  with formation of amidomercaptan. Mercaptomethylthiazoline, when treated in a similar manner, yields *amidopropyl- $\beta$ -mercaptan hydrochloride*,  $\text{SH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ , which crystallises in microscopic tablets and melts at  $87-88^\circ$ ; the *picrate* crystallises in compact, rhombic tablets melting at  $143-144^\circ$ ; on treatment with iodine, it yields *diamidopropylic  $\beta$ -bisulphide*, the hydrochloride of which,  $\text{C}_6\text{H}_{16}\text{S}_2\text{N}_2\cdot 2\text{HCl}$ , melts at  $213-214^\circ$ , the *picrate* forms short, thick prisms melting at  $162-163^\circ$ . A. H.

**Chemical Activity of Organic Ammonium Salts.** By WOLFGANG BRENDLER and JULIUS TAFEL (*Ber.*, 1898, 31, 2683—2686. Compare Tafel, *Abstr.*, 1898, i, 471).—*Trimethylacetonylammonium bromide*,  $\text{COMe}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Br}$ , obtained on passing trimethylamine into an ethereal solution of bromacetone, crystallises in well-formed, colourless needles when the alcoholic solution is exposed to an atmosphere of ether; it melts at  $190^\circ$ , and at  $195^\circ$  gives rise to a yellow distillate and tetramethylammonium bromide. The *phenylhydrazone* is a crystalline substance which dissolves more readily in water than in alcohol; Fehling's solution precipitates a yellow oil which is volatile in steam.

*Bromacetonyltrimethylammonium bromide*,  $\text{C}_6\text{H}_{13}\text{NOBr}_2$ , obtained by the action of bromine on trimethylacetonylammonium bromide,

crystallises from alcohol. If bromine water is employed instead of the undiluted halogen, a reddish-yellow, crystalline precipitate is formed having the properties of an ammonium tribromide; when an attempt is made to dry this substance, hydrogen bromide is eliminated, and bromacetyltrimethylammonium bromide is formed. The aqueous solution of the last-named substance yields trimethylamine when heated. M. O. F.

**Propylnitramine and its Alkyl Derivatives, and the Probable Existence of a New Class of Neutral Nitramines.** By HERM. UMBGROVE and ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1898, 17, 270—286).—*Dipropyldinitroxamide*,  $C_2O_2(NPr \cdot NO_2)_2$ , prepared by leaving dipropylamide in contact with six times its weight of concentrated nitric acid for 48 hours, and pouring the product into ice cold water, crystallises from alcohol in large tables, and melts at  $44^\circ$ . When dissolved (65 grams) in concentrated aqueous ammonia (150 c.c.), oxamide separates, whilst the ammonium derivative of propylnitramine remains dissolved; on adding dilute sulphuric acid to the clear solution, nearly the theoretical quantity of propylnitramine is obtained.

*Ethylpropylnitramine*, prepared by boiling a mixture of the potassium derivative of ethylnitramine (26 grams), propylic iodide (32 grams), and methylic alcohol (100 c.c.) during 30 hours, is a colourless liquid with a characteristic odour; it boils at  $108^\circ$  under a pressure of 22 mm., and has a sp. gr. = 1.028 at  $15^\circ$ . It dissolves in concentrated sulphuric acid without evolution of gas, giving rise, apparently, to nitrosulphuric acid and a substance possessing cupric-reducing power, which is probably a hydroxylamine or an imine. From the lower fractions obtained in purifying the crude ethylpropylnitramine by fractional distillation, a *substance* isomeric with the latter was isolated, differing from it in boiling point ( $65^\circ$  under a pressure of 20 mm.) and in its behaviour with concentrated sulphuric acid. On heating ethylpropylnitramine with 10 per cent. aqueous potash for 9 hours at  $150$ — $160^\circ$ , it is decomposed into propylamine, nitrous acid, and acetaldehyde; this is in accordance with van Erp's views (*Abstr.*, 1895, i, 590; and 1897, i, 6) regarding the action of alkalis on mixed aliphatic nitramines. It appears that, in this decomposition, the heavier radicle separates combined with the amido-group, and the lighter in the form of an aldehyde.

The principal product formed on leaving the silver derivative of propylnitramine (82 grams) in contact with ethylic iodide (60 grams) dissolved in ether (500 grams) during 12 hours in the dark, and subsequently heating the mixture during 6 hours at  $50^\circ$ , is *iso-ethylpropylnitramine*; this distils unchanged at  $58.5^\circ$  under a pressure of 16 mm., has a sp. gr. = 0.9755 at  $15^\circ$ , and does not give a coloration with an acetic acid solution of  $\alpha$ -naphthylamine, either alone or in presence of zinc. It differs in this respect from an isomeric *substance* formed simultaneously, which decomposes when distilled into nitrogen, water, acetaldehyde and propaldehyde; together with this unstable isomeric, a small quantity of ethylpropylnitramine is also formed. On heating *iso-ethylpropylnitramine* with 10 per cent. aqueous potash,

nitrogen is evolved, and propaldehyde appears to be formed, although this immediately polymerises, giving a resin.

*Isopropylethylnitramine*, prepared by acting on the silver derivative of ethylnitramine with an ethereal solution of propylic iodide, boils at 65° under a pressure of 20 mm., and has a sp. gr. = 0.9783 at 15°; at the same time, propylethylnitramine is formed, together with an isomeric substance, which decomposes when heated, giving nitrogen and propaldehyde.

When isopropylethylnitramine is heated with 10 per cent. aqueous potash, it gives rise to nitrogen and acetaldehyde, in accordance with van Erp's rule (*loc. cit.*).

*Isopropylmethylnitramine*, prepared by leaving the silver derivative of methylnitramine in contact with propylic iodide dissolved in ether during 5 days at the ordinary temperature, boils at 51° under a pressure of 18 mm., and has a sp. gr. = 1.012 at 15°; although no gas is evolved when it is heated at 100°, it gives a marked coloration with an acetic acid solution of  $\alpha$ -naphthylamine. When decomposed by aqueous potash, it apparently gives rise to formaldehyde.

W. A. D.

**Action of Sulphuric Acid on Aliphatic Nitramines and their Isomerides.** By ANTOINE P. N. FRANCHIMONT and HERM. UMBGROVE (*Rec. Trav. Chim.*, 1898, 17, 287—295).—Concentrated sulphuric acid acts in the same manner on the silver and mercury derivatives of methylnitramine as on methylnitramine itself; in each case, nearly the theoretical quantity of nitrous oxide is evolved, no other gas being formed. From ethylnitramine, however, and its potassium derivative, a small quantity of an inflammable gas, probably an olefine, was also obtained, and the same is true of propyl- and butyl-nitramine.

The behaviour of ethylpropylnitramine with concentrated sulphuric acid has been dealt with in the preceding abstract; the action is the same, but slower, when 40 per cent. sulphuric acid is employed, partial decomposition only taking place. The isodialkylnitramines are, however, rapidly decomposed by this acid at the ordinary temperature, giving nitrous oxide and two alcohols, that formed by the alkyl radicle directly attached to the nitrogen also giving rise, as a rule, to an olefine, except in the case when the radicle is methyl. This behaviour was verified in the case of iso-ethylmethyl-, isomethylethyl-, isodiethyl-, iso-ethylpropyl-, isopropylethyl-, and isopropylmethylnitramines. The ease with which the isodialkylnitramines undergo decomposition when treated with 40 per cent. sulphuric acid is explained by attributing to them the general formula  $\text{NR}:\text{NO}\cdot\text{OR}$ ; or, assuming

that the acid nitramines have the general formula  $\text{O} \begin{array}{c} \text{NHR} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{O}$  (Brühl), by giving the neutral isonitramines the general structure  $\text{O} \begin{array}{c} \text{NR} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \cdot \text{OR}$ .

W. A. D.

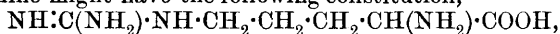
**Neurine and its Derivatives.** By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1898, 26, 175—188).—The author describes the appearance, as seen with the unassisted eye and with the microscope, of

precipitates obtained with dilute solutions of synthetically prepared neurine hydrochloride and the usual reagents for alkaloids. These precipitates obtained with dilute solutions of neurine are far less soluble than those from choline. Contrary to Brieger's observation, the author finds that phosphotungstic acid gives a precipitate with neurine hydrochloride which is distinctly visible even in solutions containing only  $\frac{1}{2000}$ th of the base.

Neurine picrate forms golden-yellow needles melting at  $263-264^{\circ}$ ; it is very insoluble in cold water and alcohol. Neurine platinochloride melts at  $195.5-198^{\circ}$ , contains no combined water, and differs in its crystalline form from the corresponding choline salt. The aurichloride,  $C_5H_{12}NAuCl_4$ , forms golden-yellow needles melting at  $228-232^{\circ}$ , and contains no water of crystallisation. On the addition of mercurous chloride to an alcoholic solution of neurine hydrochloride, two double salts are precipitated; the less soluble,  $C_5H_{12}NCl \cdot 6HgCl_2$ , forms colourless, tabular crystals and melts at  $230.5-234^{\circ}$ ; the more soluble,  $C_5H_{12}NCl \cdot HgCl_2$ , crystallises in aggregates of narrow prisms and melts at  $198.5-199.5^{\circ}$ . Dilute solutions of neurine are not decomposed on boiling, but concentrated solutions give off trimethylamine. Neurine hydrochloride, when recrystallised from water, has no tendency to take up one molecule of the solvent and become transformed into choline hydrochloride.

G. T. M.

**Constitution of Ornithine and Arginine.** By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1898, **26**, 1-14. Compare Abstr., 1898, i, 281).—Ornithine,  $C_5H_{12}N_2O_2$ , was originally discovered by Jaffé (Abstr., 1878, 585), who suggested that its constitution might be that of a diamidovaleric acid; it does, in fact, closely resemble the diamidopropionic acid prepared synthetically by E. Klebs (Abstr., 1894, i, 439). Arginine,  $C_6H_{14}N_4O_2$ , prepared either from the seedlings of *Lupinus luteus* or by heating albumin with hydrochloric acid, yields ornithine and carbamide when hydrolysed with baryta water. Ornithuric acid, the dibenzoyl derivative of the former base (Jaffé, *loc. cit.*), is obtained from the crude product of reaction by the Schotten-Baumann method; this compound is hydrolysed by concentrated hydrochloric acid, first into a monobenzoyl derivative, and then into ornithine, the yield of benzoic acid and ornithine dihydrochloride being almost theoretical. Ornithine, on treatment with nitrous acid, loses the whole of its nitrogen, but the hydroxy-acid which should be formed has not been investigated. Phenanthraquinone gives no quinoxaline derivative with ornithine, and the authors therefore suppose that the amidogen groups are not attached to contiguous carbon atoms. If ornithine be assumed to be a diamidovaleric acid, then arginine might have the following constitution,



which resembles those of glycocyamine and creatine.

The yield of ornithine from arginine is only 40 per cent. of the theoretical quantity. This may be due, as in the case of creatine, to the fission of the molecule taking place in two ways, but no other well-characterised product of hydrolysis has yet been isolated.

G. T. M.

**The So-called Nitroazoparaffins.** By EUGEN BAMBERGER (*Ber.*, 1898, 31, 2626—2635).—In accordance with modern views, the “nitroazoparaffins” of Victor Meyer must be regarded as hydrazones containing the grouping  $\cdot\text{C}(\text{NO}_2):\text{N}\cdot\text{NH}\cdot$ , and, therefore, as true nitro-compounds, whilst their salts must be looked on as derived from the tautomeric isonitro-azo-compounds, the above group having become  $\cdot\text{C}(\text{NOOH})\cdot\text{N}\cdot\text{N}\cdot$ .

When “nitroazoparaffins” are subjected to alkaline hydrolysis, they are decomposed with production of acylhydrazines and nitrous acid. Thus “phenyl-nitroazopropane,” or nitropropionalde(phenyl)-hydrazone,\* as the author prefers to term it, when heated on the water-bath, with a 1 per cent. solution of soda, is almost quantitatively converted into  $\beta$ -propionylphenylhydrazine, probably in accordance with the equation,  $\text{NO}_2\cdot\text{C}^{\text{Et}}\cdot\text{N}\cdot\text{NHPh} + \text{H}_2\text{O} = \text{COEt}\cdot\text{NH}\cdot\text{NHPh} + \text{HNO}_2$ .

*Nitroacetalde(phenyl)hydrazone*,  $\text{NO}_2\cdot\text{C}^{\text{Me}}\cdot\text{N}\cdot\text{NHPh}$ , is produced in nearly theoretical amount by the foregoing process. Nitroethane (10 grams) is quickly dissolved in an ice cold solution of soda (5.2 grams) in water (3 grams) and mixed at once with an ice cold solution of the diazonium acetate made by dissolving aniline (12 grams), concentrated hydrochloric acid (30 grams), sodium nitrite (9.4 grams), and crystallised sodium acetate (44.4 grams) in water (2 litres). The substance separates quickly as a yellow oil, which soon solidifies; it does not exhibit either Meyer’s or Konowaloff’s reaction, and cannot, therefore, be the “iso-” form,  $\text{NOOH}\cdot\text{C}^{\text{Me}}\cdot\text{N}\cdot\text{NPh}$ . It crystallises from alcohol in golden-yellow, and from benzene in orange-red, leaflets, and melts at  $141\text{--}142^\circ$ . It decomposes slightly when kept in a closed vessel, and then has an odour of acetic acid; in one instance, it decomposed, giving nitrous and acetic acids and diazobenzene nitrate.

When nitroacetalde(phenyl)hydrazone is warmed with a dilute solution of soda in dilute methylic alcohol for 2 hours, it is decomposed, giving an appreciable quantity of an isodiazotate, ammonia, phenylhydrazine, and a neutral oil, but the principal product is  $\beta$ -acetyl-phenylhydrazine.

Nitropropionalde(phenyl)hydrazone,  $\text{NO}_2\cdot\text{C}^{\text{Et}}\cdot\text{N}\cdot\text{NHPh}$ , prepared by a method similar to that used in the case of the acetaldehyde compound, forms hard, orange-yellow crystals, and melts at  $98.5\text{--}99.5^\circ$  (compare Meyer, this Journal, 1876, ii, 93). It does not, as stated by Meyer, give an immediate violet-red coloration when treated with strong sulphuric acid, but a fiery-red, the violet tone being a later development; a similar statement holds true in the case of the acetaldehyde compound. Nitropropionalde(phenyl)hydrazone, is, as has already been mentioned, almost completely converted into nitrous acid and  $\beta$ -propionylphenylhydrazine when warmed with dilute soda.

*Nitrovaleralde(phenyl)hydrazone*,  $\text{C}_4\text{H}_9\cdot\text{C}(\text{NO}_2):\text{N}\cdot\text{NHPh}$ , is obtained when nitropentane is treated with the diazonium acetate; it exists in two forms. The  $\beta$ -modification obtained by crystallising the substance from alcohol, separates in golden-yellow leaflets having a bronze-like lustre, and melts at  $92.5\text{--}93^\circ$ , dissolves readily in acetone, and decomposes when kept for a long time in a closed vessel; its solution in sulphuric acid is at first fiery red, but gradually becomes violet-red

\* The author omits the “phenyl” in his paper.—[EDITORS.]

spontaneously, and at once on the addition of dichromate. The  $\alpha$ -modification obtained from the former by boiling it with heavy petroleum, separates from the solution on cooling in long, silky needles, which are orange-red by reflected and golden-yellow by transmitted light, and have a metallic-blue reflex; it has the same composition as the  $\alpha$ -form, but melts at  $51.5-52^\circ$ , and is very readily dissolved by light petroleum; it may be converted into the  $\beta$ -modification by dissolving it in boiling alcohol, and if the melted substance is allowed to solidify, it melts once more at  $86-87^\circ$ , indicating a more or less complete conversion into the  $\beta$ -form; a similar change is found to have occurred when its solution in alkalis is precipitated by means of an acid. By treatment with alkali,  $\beta$ -nitrovaleralde(phenyl)hydrazone is converted into  $\beta$ -valerophenylhydrazide; the latter melts at  $112-112.5^\circ$  and not at  $101^\circ$  as stated by Autenrieth (Abstr., 1888, 251). A. L.

**Formhydroxamic Acid.**—By JOHN U. NEF (*Ber.*, 1898, 31, 2720—2721).—In view of the paper recently published by Schroeter (Abstr., 1898, i, 623), the author points out that investigations on formhydroxamic acid and its derivatives are in progress in his laboratory. The ethers of this acid can be obtained by heating formic acid with  $\alpha$ -alkylhydroxylamines. Benzylhydroxamic acid, for example, can readily be prepared in this way, and is a thick oil with strongly acid properties. A. H.

**Action of Semicarbazide on Formaldehyde.** By JOHANNES THIELE and JAMES BAILEY (*Annalen*, 1898, 303, 91—93).—When a 4 per cent. solution of formaldehyde is added to aqueous semicarbazide hydrochloride, a gelatinous precipitate is formed, and this compound, after being washed with water and dried at  $95^\circ$ , has the composition  $C_5H_{10}N_6O_2 + \frac{1}{2}H_2O$ ; it is, therefore, a hydrated condensation product of semicarbazide (2 mols.) with formaldehyde (3 mols.). H. Thoms (*Ber. deutsch. Pharm. Ges.*, 7, 5) has recently obtained a normal product of condensation. The substance dissolves in 60 per cent. hydrocyanic acid, yielding a compound which crystallises from dilute acetic acid, and melts at  $127.5^\circ$ ; no definite formula has been assigned to it. M. O. F.

**Aldehyde-ammonia.** By ROBERT DE FORCRAND (*Compt. rend.*, 1898, 126, 248—250).—The author's calorimetric experiments confirm those by which Delépine (Abstr., 1898, i, 462) demonstrates that aldehyde-ammonia in the solid state consists of the more or less polymerised hydrate of ethylidenimine, and that, when dissolved in water, a gradual change into the simple form takes place.

Two series of calorimetric determinations were made on the heat developed by the action of dilute sulphuric acid on solutions of aldehyde-ammonia which had been kept for different periods of time.

In one case, the aldehyde-ammonia solution was prepared by adding weak ammonia to a dilute solution of aldehyde, and in this series of determinations the heat effect at first decreased until a minimum was reached after 8 days, and then increased until the end of 50 days.

When the solution was prepared by dissolving solid aldehyde-ammonia in water, the heat developed by the action of the acid was

least after 7 minutes, and gradually increased until the end of 50 days. In the first series, there is a rapid change of aldehyde-ammonia into polymerised ethylidenimine, and, at the same time, this polymeride slowly passes into the simple form; in the second series, the polymeride gradually dissociates into the simple imine. G. T. M.

**Amidoaldehydes.** By EMIL MAASS and RICHARD WOLFFENSTEIN (*Ber.*, 1898, 31, 2687—2692. Compare Abstr., 1898, i, 44).—For reasons which are discussed in the original paper, the authors regard those amidoaldehydes which are convertible into piperidine derivatives as capable of acting in accordance with the tautomeric formula,  $C_5H_8 \cdot NH \cdot O$ ; from this point of view, they belong to the group of oxides obtained by the action of hydrogen peroxide on 1-alkylpiperidine bases (Wernick and Wolffenstein, Abstr., 1898, i, 536). The facts which have led to this conclusion are as follows.

The benzoyl derivative of orthamidomethylphenylacetaldehyde (Abstr., 1898, i, 44) yields benzoic acid on oxidation with potassium permanganate. Benzoic acid is also produced by the oxidation of the benzoyl derivative of  $\delta$ -amidovaleraldehyde (Abstr., 1892, 1484), which melts at  $66^\circ$ ; the other product is a hygroscopic syrup which is also formed when piperidine is oxidised with potassium permanganate. Carbon bisulphide converts  $\delta$ -amidovaleraldehyde into the dithiocarbamate of piperidine (m. p.  $169$ — $171^\circ$ ), and by its action on amidovaleropropanaldehyde, gives rise to the dithiocarbamate of coniine, which melts at  $58$ — $61^\circ$ .

In the behaviour of amidovaleraldehyde towards nitrous acid, however, it resembles ordinary amidoaldehydes. M. O. F.

**Action of Water on Acraldehyde Dibromide.** By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1898, 17, 259—262).—Although acraldehyde dibromide is converted into bromacraldehyde when boiled with a 50 per cent. aqueous solution of sodium acetate (Piloty and Stock, Abstr., 1898, i, 402), it apparently gives rise to *glyceraldehyde* when left in contact with water, either at the ordinary temperature, or, better, at that of the water-bath. On removing the hydrobromic acid from the solution by successive treatment with lead carbonate, hydrogen sulphide, and moist silver oxide, and subsequently concentrating in a vacuum, a syrup is obtained which reduces Fehling's solution, and gives rise to glycerosazone when mixed with a solution of phenylhydrazine acetate. W. A. D.

[NOTE BY ABTRACTOR.—Since the original paper was published, Wohl (*Ber.*, 1898, 31, 2394) has prepared glyceraldehyde from the acetal of acraldehyde, in the form of a white, crystalline powder.]

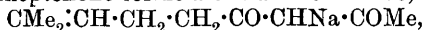
**Acetylmethylheptenone (2 Methyl-2-nonene-6:8-dione).** By PHILIPPE BARBIER and GEORGES LESER (*Bull. Soc. Chim.*, 1897, [iii], 17, 748—751).—Natural methylheptenone (2-methyl-2-heptene-6-one) readily reacts with ethylic acetate in the presence of sodium, with the formation of *acetylmethylheptenone*,  $CM_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot COMe$ . The latter is purified by conversion into its copper derivative, a pale



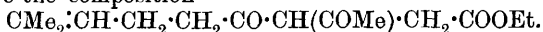
blue, crystalline powder melting at 132—133°, from which it is regenerated by the action of dilute sulphuric acid. Acetylmethylheptenone is a colourless liquid of powerful aromatic odour and having a sp. gr. = 0.954 at 0°. It boils at 114—115° under a pressure of 15 mm., and at 233—234°, with slight decomposition, at the ordinary pressure. Treatment with the theoretical quantities of hydroxylamine hydrochloride and sodium carbonate converts it into the *oxazole*,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{CMe} \\ \text{N}-\text{O} \end{smallmatrix}$ , which boils at 118—119° under a

pressure of 14 mm., whilst the *dioxime*, a crystalline substance melting at 109—110°, is also formed.

Acetylmethylheptenone forms a sodium derivative,



which, when warmed for some hours with ethylic monochloracetate, is converted into a mixture of the ethylic salts of 2-methyl-2-hexenoic acid, levulinic acid, and 2-methyl-2-nonene-6-onoic acid. The first two of these compounds are formed by the action of alcohol, and the third by the action of water, on the normal product of the reaction, which would have the composition



*Ethylic 2-methyl-2-hexenoate*,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOEt}$ , is a colourless liquid of agreeable odour which boils at 182—184° and has a sp. gr. = 0.928 at 0°. On hydrolysis, it yields *2-methyl-2-hexenoic acid*, which is a colourless liquid boiling at 216—218°.

*Ethylic 2-methyl-2-nonene-6-onoate* boils at 152—154° under a pressure of 14 mm. and has a sp. gr. = 0.988 at 0°. The corresponding *acid* crystallises from light petroleum in colourless needles melting at 57°. The ethylic salt forms a *phenylhydrazone*, which melts at 93° and boils at 235—240° under a pressure of 15 mm.

The sodium derivative of acetylmethylheptenone reacts with ethylic iodide to form *acetylmethylethylheptenone*, which boils at 133—135° under a pressure of 15 mm. N. L.

**Conversion of Ketones into Diketones. III.** By MICHELE FILETI and GIACOMO PONZIO (*J. pr. Chem.*, 1898, [ii], 58, 362—367).—Further investigations have confirmed the conclusions already arrived at (*Abstr.*, 1897, i, 317).

Ethyl butyl ketone yields a mixture of two diketones, *acetylvaleryl* and *propionylbutyryl*, and two dinitrohydrocarbons; of the former, the mixture of *dioximes* was so far separated by fractional crystallisation from dilute alcohol that fractions melting at 168—170° and 141—144° were obtained; as regards the dinitrohydrocarbons, potassiodinitroethane is more soluble than the corresponding butane derivative. Ethyl amyl ketone behaves in a similar manner; acetylhexoyl and propionylvaleryl are the diketones; the *dioxime* and *osazone* of the latter melt at 139—141° and 96—97° respectively; as regards the dinitrohydrocarbons, potassiodinitroethane is more soluble than the corresponding pentane derivative. Ethyl isoamyl ketone yields acetylisoheptyl and dinitroethane only; the *dioxime* of the former was also prepared from ethylic isoamylacetate. Ethyl isoheptyl ketone yields acetylisoamylacetyl and dinitroethane only. C. F. B.

**Acetylation with the help of Sulphuric Acid.** By ZDENKO H. SKRAUP (*Monatsh.*, 1898, 19, 458—460).—The author points out that Franchimont (Abstr., 1880, 159) was the first to draw attention to the value of sulphuric acid as an addition to acetic anhydride in acetylating (compare Thiele, Abstr., 1898, 469), and the method has long been employed in the author's laboratory. The reaction is liable to become uncontrollable unless precautionary measures are taken.

By the action of acetic anhydride containing less than 1/100 per cent. of its weight of sulphuric acid on mucic acid, tetracetylmucic acid is easily produced in amount equal to 79 per cent. of that theoretically possible. By the usual method of heating the acid with acetic anhydride and anhydrous sodium acetate, only amorphous products are obtained. With smaller quantities of sulphuric acid (1/10000 per cent.), the reaction still goes on, but is probably incomplete.

The method of estimating acetyl used by Wenzel (Abstr., 1898, i, 234) was published first by Franchimont (*Ber.*, 1879, 12, 1940), and modified later by the author (Abstr., 1894, i, 15). A. L.

**Preparation of Zinc Valerate.** By DIOSCORIDE VITALI (*L'Orosi*, 1898, 21, 114—117).—One hundred parts of dry sodium valerate and 117 parts of crystallised zinc sulphate are separately dissolved in the smallest possible quantity of hot water, the solutions mixed, the liquid evaporated to dryness at a temperature not exceeding 70°, and the finely powdered residue extracted with 95 per cent. alcohol. On concentrating the alcoholic extract by evaporation at 70°, zinc valerate is obtained in a very pure crystalline condition. This process is simpler and more economical than those commonly employed.

N. L.

**Wax of the Humble Bee.** By ERNST E. SUNDVIK (*Zeit. physiol. Chem.*, 1898, 26, 56—59).—Samples of wax taken from the nests of *Bombus muscarum* and *B. lapidarius* have the same chemical properties. The mixture of wax and pollen, freed from eggs and larvæ, and extracted with ether or chloroform, yields a crude wax of brownish-yellow colour, melting at 35—40°, and having an agreeable odour resembling honey. This substance still contains fat and colouring matter. The principal constituent of the wax is an alcoholic substance, which is freed from glycerides by treating the partly purified product with weak potash on the water-bath. After repeated crystallisations from alcohol, the unaltered residue melts at 74—75°, and its composition agrees with the formula  $C_{34}H_{70}O$ ; it forms flexible, woolly needles which can be easily kneaded into a pale yellow cake. A benzoyl derivative,  $C_{34}H_{69}OBz$ , obtained by heating the substance with benzoic anhydride at 150—160°, crystallises from alcohol, benzene, and petroleum, and melts at 55°.

G. T. M.

**Ethylic  $\beta$ -Isopropylacetobutyrate and Stereoisomeric Di-isopropylbutenedicarboxylic Acids.** By PHILIPPE BARBIER and V. GRIGNARD (*Compt. rend.*, 1898, 126, 251—253).—Ethylic isobutylideneacetoacetate and ethylic malonate suffer condensation in the presence of potassium ethoxide, yielding a liquid which, when

distilled, first under ordinary and subsequently under reduced pressure, gives rise to two substances; the chief product, a colourless liquid boiling at  $170^{\circ}$  under atmospheric pressure, consists of *ethylic  $\beta$ -isopropylacetobutyrate*,  $\text{CH}_2\text{Ac}\cdot\text{CHPr}^{\beta}\cdot\text{CH}_2\cdot\text{COOEt}$ ; the product obtained in less quantity is an unstable intermediate *compound*,  $\text{COOEt}\cdot\text{CHAc}\cdot\text{CHPr}^{\beta}\cdot\text{CH}(\text{COOEt})_2$ , boiling at  $189\text{--}191^{\circ}$  under a pressure of 10 mm., which passes into the preceding substance by the loss of two COOEt groups.

When ethylic  $\beta$ -isopropylacetobutyrate is treated with sodium ethoxide, two molecules of the former coalesce, and condensation takes place, accompanied by the elimination of two molecules of acetone. The *ethereal salt*,  $\text{C}_{16}\text{H}_{28}\text{O}_4$ , which is obtained, boils at  $156^{\circ}$  under a pressure of 10 mm., and on hydrolysis furnishes a mixture of two isomeric *di-isopropylbutenedicarboxylic acids*, having the formula  $\text{COOH}\cdot\text{CH}_2\cdot\text{CPr}^{\beta}\cdot\text{CPr}^{\beta}\cdot\text{CH}_2\cdot\text{COOH}$ ; one crystallises in needles melting at  $156\text{--}158^{\circ}$ , the other in colourless plates melting at  $117\text{--}119^{\circ}$ . The stereoisomeric relationship of these isomerides has not yet been determined.

G. T. M.

**Syntheses with Ethylic Cyanacetate.** By TIMOTHÉE KLOBB (*Ann. Chim. Phys.*, 1897, [vii], 10, 145—214).—*Ethylic isovalerylcyanacetate*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$ , produced by adding an ethereal solution of isovaleric chloride to an alcoholic solution of ethylic cyanacetate in the presence of sodium ethoxide, separates in white needles when the oily product is cooled to  $-36^{\circ}$ ; it melts at  $+21^{\circ}$ , boils at  $138\text{--}140^{\circ}$  under a pressure of 21 mm., at  $144\text{--}148^{\circ}$  under 31 mm., and decomposes when distilled at the ordinary pressure; its specific gravity = 1.030 at  $24^{\circ}$ . The substance is a strong acid, not only decomposing carbonates, but its alcoholic solution dissolves the metals, magnesium, zinc, iron, aluminium, copper, cobalt, and nickel, with the evolution of hydrogen; silver, bismuth, and antimony are not attacked. The *magnesium, ferrous, and copper* derivatives obtained in this manner by the displacement of the hydrogen in the CH group are described.

*Methylic isovalerylcyanacetate*, prepared like the ethylic salt, crystallises in rhombic plates melting at  $41\text{--}42^{\circ}$ , and boils without decomposition at  $171\text{--}172^{\circ}$  under a pressure of 100 mm.; its *sodium, calcium, barium, and silver* derivatives are crystalline. Both ethereal salts are insoluble in water, but dissolve easily in the usual organic solvents.

When boiled with aqueous potash, they undergo hydrolysis, ammonia, the potassium salts of carbonic, acetic, and isovaleric acids and the corresponding alcohol being produced; long continued boiling with water results in the formation of tarry products and a small quantity of a *compound* having the formula  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}$ , and crystallising in white needles melting at  $133\text{--}134^{\circ}$ .

The preparation of the alkylic derivatives of diphenacylcyanacetic acid ( $\beta\beta$ -dibenzoylcyanisobutyric acid) is given in detail; the *propylic* salt, obtained by the action of bromacetophenone on methylic cyanacetate, dissolved in propylic alcohol, in the presence of sodium propyloxide, crystallises from alcohol in nacreous leaflets and melts at  $114^{\circ}$ . The isobutylic salt could not be obtained by this method; the

methylic and ethylic salts have been previously described (see Abstr., 1894, i, 592; 1897, i, 531). Phenylhydrazine gives rise to no definite hydrazones with these ethereal salts. On hydrolysis with boiling alkalis, they yield diphenacylacetic acid ( $\beta\beta$ -dibenzoylisobutyric acid).

The preparation of the alkylic phenacylcyanacetates ( $\alpha$ -cyano- $\beta$ -benzoylpropionates) is described at some length; an account of these compounds and of the free acid has already been published (see Abstr., 1896, i, 126).  $\beta$ -Benzoylpropionic acid is the final product of the action of potash on these ethereal salts.

The syntheses based on the displacement of the hydrogen of the group CH in the above ethereal salts have already been studied (Abstr., 1896, *loc. cit.*, and 1897, i, 419; 1898, i, 586); the preparation of the methylic, ethylic, and benzylic substitution products are fully described in the paper. Ethylic and methylic  $\alpha$ -cyano- $\beta$ -acetylpropionates have already been described (Abstr., 1896, *loc. cit.*).  
G. T. M.

**Constitution of Tetric Acid and of the Lactone of  $\gamma$ -Hydroxydimethylacetoacetic Acid.** By MAX CONRAD and RICHARD GAST (*Ber.*, 1898, 13, 2726—2731).—Methylic monobromodimethylacetoacetate, which has been previously described (Abstr., 1897, i, 321), boils at 225—230° under atmospheric pressure, undergoing slight decomposition. When the acetate prepared from this compound by means of potassium acetate is kept for some months at the ordinary temperature, it yields methylic acetate and the lactone of  $\gamma$ -hydroxydimethylacetoacetic acid (2:2-dimethyl-3-butanone-4-olonic acid,  $\text{CMe}_2 \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ , which is a colourless oil of sp. gr. = 1.147 at 18°/15°, and boils at 208—212° without decomposing. The dilute alcoholic solution gives no reaction with ferric chloride. Bromine converts the lactone into a *monobromo*-derivative, which is decomposed by water with formation of the lactone of dihydroxydimethylacetoacetic acid. Aniline converts the original lactone into a *derivative*,  $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$ , which crystallises in compact, lozenge-shaped crystals melting at 88° and boiling at 300—310°; this compound, which is decomposed by aqueous baryta and by platinic chloride, probably has the constitution  $\text{CMe}_2 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \text{C}(\text{NPh}) \end{smallmatrix} \text{CH}_2$ . The lactone readily reacts with hydroxylamine hydrochloride to form an *oximidolactone*,  $\text{OH} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{CMe}_2 \cdot \text{CO} \end{smallmatrix}$ , which melts at 134°, and gives no coloration with ferric chloride; the corresponding *phenylhydrazone* melts at 131°, and is sparingly soluble in light petroleum. *Methylic tetratate*,  $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{CMe} \cdot \text{CO} \end{smallmatrix}$ , prepared by the action of methylic iodide on silver tetratate, is a colourless liquid boiling at 215—220°; it is isomeric with the lactone just described, but does not yield derivatives with hydroxylamine or phenylhydrazine, whilst acids reconvert it into tetric acid.

The fact that the lactone of  $\gamma$ -hydroxydimethylacetoacetic acid is so

dissimilar from tetric acid both in chemical behaviour and boiling point renders it improbable that the latter is the lactone of  $\gamma$ -hydroxy-methylacetoacetic acid, having the formula



**Reduction of Aconic Acid to Paraconic Acid.** By HANS REITTER (*Ber.*, 1898, 31, 2722—2725).—Aconic acid is readily converted into paraconic acid when it is treated with glacial acetic acid and zinc dust, although Fittig (*Annalen*, 1883, 216, 97) was unable to effect this reduction by means of sodium amalgam. The ready formation of paraconic acid affords further evidence in favour of the formula  $\text{COOH} \cdot \text{C} \begin{array}{l} \diagup \text{CH} - \text{O} \\ \diagdown \text{CH}_2 \cdot \text{CO} \end{array}$  for aconic acid proposed by Fittig.

A. H.

**Synthesis of Terebic Acid.** By EDMOND E. BLAISE (*Compt. rend.*, 1898, 126, 349—351).—Ethylic bromosuccinate and acetone are mixed together in the presence of a copper-zinc couple and the mixture is occasionally shaken during 24 hours. The double zinc compound produced is decomposed by dilute sulphuric acid, and the ethylic terebate is extracted by means of ether and hydrolysed by aqueous potash. The acid is liberated by hydrochloric acid and purified, first by conversion into its soluble barium salt, and subsequently by recrystallisation from water and alcohol; it melts at  $174^\circ$ , and is further identified by conversion into methyl-2-pentanolide. The yield of terebic acid from ethylic bromosuccinate is 10—12 per cent., that from pinene is less than 2.

G. T. M.

**Tautomeric Forms of Ethylic Isaconitate and of Ethylic Dicarboxyglutaconate.** By MAX GUTHZEIT (*Ber.*, 1898, 31, 2753—2758).—Ethylic isaconitate is a thin, colourless liquid which boils at  $178$ — $180^\circ$  under a pressure of 20 mm. and has the sp. gr. = 1.1291 at  $20^\circ/20^\circ$ .

This constitutes the enolic form of the compound, and gives a deep blue coloration with ferric chloride, whilst it also forms a copper salt, and is at once coloured deep yellow by sodium carbonate. This form is always obtained by the ordinary methods of preparation, but changes very slowly, if kept, into the ketonic or true form, which is also produced in a few hours when a small amount of piperidine is added to the enolic form.

The ketonic form is a very viscid, deep yellow oil which cannot be distilled without undergoing decomposition, and has a sp. gr. = 1.1432 at  $20^\circ/20^\circ$ . It gives no coloration with ferric chloride, does not yield a copper salt, and is only slowly coloured yellow by sodium carbonate. When it is dissolved in alcoholic sodium ethoxide and the solution acidified, the enolic form is regained. Both forms have the same molecular weight as determined by the boiling point method.

The two forms of this compound probably have the following constitutions,

$\text{COOEt} \cdot \text{CH} : \text{CH} \cdot \text{CH}(\text{COOEt})_2$ ;  $\text{COOEt} \cdot \text{CH} : \text{CH} \cdot \text{C}(\text{COOEt}) : \text{C}(\text{OH}) \cdot \text{OEt}$   
Ethylic dicarboxyglutaconate appears also to exist in two forms, the enolic form being that which has previously been described, whilst the

ketonic or true form, which is produced by the action of piperidine and is also formed when the enolic form is kept for a long time, crystallises in monosymmetric crystals melting at 101—102°. The latter have only been obtained in very small amount, and are being further investigated. A. H.

**Condensation of Ethylic Malonate with Aldehydes under the Influence of Ammonia and Organic Amines.** By EMIL KNOEVENAGEL (*Ber.*, 1898, 31, 2585—2595. Compare Abstr., 1894, i, 570, &c.)—Methylenebispiperidine and methylenebisaniiline react readily with ethylic malonate when heated with it on the water-bath, yielding ethylic methylenebismalonate. When aniline is added to ethylic malonate mixed with formaldehyde, no action takes place at the ordinary temperature, and methyleneaniline does not react with ethylic malonate to form ethylic methylenebismalonate. The best method for the production of the latter substance is to add a small quantity of an amine, usually piperidine or diethylamine, to a mixture of formaldehyde and ethylic malonate mixed in the requisite proportions.

Ethylic ethyліденebismalonate, prepared in a manner similar to the above, boils at 208—209° under a pressure of 17 mm.; it is accompanied by ethylic ethyліденemalonate. The derived  $\beta$ -methylglutaric acid melts at 87°, and its anhydride at 47°. *Ethylic isobutylidenebismalonate* boils at 198° under a pressure of 12 mm., and  $\beta$ -isopropylglutaric acid prepared from it melts at 96·5—97° (Schryver, *Trans.*, 1893, 1345, gives 99—100°), and affords a silver salt,  $C_8H_{12}O_4Ag_2$ , which is sparingly soluble in water. *Ethylic  $\beta$ -isopropylglutarate* is a thick oil having a pleasant odour, and boils at 250° under atmospheric pressure.

*Ethylic isoamylidenebismalonate*,  $C_{19}H_{32}O_8$ , boils at 204° under a pressure of 15 mm.  $\beta$ -isobutylglutaric acid crystallises in long, white needles, and melts at 48°; it is very soluble in ether, alcohol, glacial acetic acid, and water, and somewhat readily in carbon bisulphide and light petroleum; its copper, zinc, and lead salts are insoluble in water, and the silver salt,  $C_9H_{14}O_4Ag_2$ , is a white, curdy precipitate.

*Ethylic cenanthylidenebismalonate*,  $C_{21}H_{36}O_8$ , boils at 195° under a pressure of 16 mm.; the corresponding  $\beta$ -hexylglutaric acid was obtained in very small amount, and melted at 215—236°.

Aromatic aldehydes and ethylic malonate condense in molecular proportion under the influence of amines. Ethylic benzylidenemalonate is easily obtained by treating a mixture of benzaldehyde (1 mol.) and dry ethylic malonate (1 mol.), with a little piperidine or alcoholic ammonia. [With F. GIESE.]—*Ethylic cumylidenemalonate*,  $C_{17}H_{22}O_4$ , is a light yellow oil, and boils at 205—208° under 15 mm. pressure.

[With H. HOFFMANN.]—*Ethylic paranitrobenzylidenemalonate*,  $C_{14}H_{14}O_6N$ , forms colourless needles and melts at 94°; it dissolves readily in hot alcohol, light petroleum, and benzene, but only sparingly in ether.

Ethylic coumarincarboxylate,  $\begin{array}{c} C(COOEt):CH \\ \diagup \quad \diagdown \\ CO \quad \quad \quad O \end{array} > C_6H_4$ , is made by the condensation of salicylic aldehyde with ethylic malonate by means

of piperidine or ammonia; it forms crystals, and melts at  $94^{\circ}$ ; coumarincarboxylic acid melts at  $185-187^{\circ}$ .

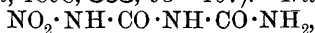
[With A. GROOS.]—*Ethylic unsylidinemalonate*,  $C_{15}H_{18}O_5$ , boils at  $200-217^{\circ}$  under 14 mm. pressure, and melts at  $38-40^{\circ}$ ; it dissolves readily in ether, benzene, and alcohol. *Ethylic methylsalicylidene-malonate*,  $C_{15}H_{18}O_5$ , boils at  $193-195^{\circ}$  under a pressure of 14 mm., and could not be solidified.

[With F. GIESE.]—*Ethylic piperonylidenemalonate* boils at  $216-219^{\circ}$  under a pressure of 11 mm., crystallises from alcohol in beautiful, colourless prisms, and melts at  $63^{\circ}$ ; it is readily soluble in cold benzene and acetic acid, and in warm ether and alcohol, and is sparingly soluble in light petroleum.

*Ethylic furfurylidenemalonate*, which may be produced in several different ways by the condensation of furfuraldehyde and ethylic malonate, is obtained in small amount by merely warming the components together on the water-bath, but the yield is greatly augmented by the addition of a little piperidine. A. L.

**Uric Acid and the Murexide Reaction.** By DIOSCORIDE VITALI (*L'Orosi*, 1898, 21, 73—80).—The fact that the presence of small quantities of iodides in urine cannot be directly demonstrated by the usual methods has been attributed to the oxidation of organic compounds, especially uric acid, by the iodine at the moment of its liberation, with simultaneous formation of hydriodic acid. The production of the latter is shown by the immediate liberation of iodine on adding iodic acid, and by means of this reagent traces of iodine in the form of iodides may readily be detected in urine. If, moreover, a solution of iodine be gradually added to a solution of potassium urate mixed with a little starch paste, no blue coloration appears until a considerable amount of iodine has been absorbed; the liquid at the same time becomes acid from the production of hydriodic acid, and deposits a crystalline precipitate of uric acid. A portion of the latter is simultaneously oxidised to carbamide and alloxan, as was proved by the isolation of urea oxalate and by the fact that the liquid gave the murexide reaction when evaporated to dryness and gently heated. This formation of murexide (ammonium purpurate) is probably due to the action of the ammonia, produced by the decomposition of the carbamide, on the alloxantin formed by the reduction of the alloxan by hydriodic acid. Instead of iodine, chlorine, bromine, iodic acid, and nitric acid may be used. In the last case, the necessary reduction in the latter phase of the reaction is, perhaps, brought about by nitric oxide or nitrous acid, but the action of chlorine is not easily explained. The use of bromine or iodine instead of nitric acid in the murexide test for uric acid is recommended as giving more certain results, with less liability to failure from excessive heating. Hypoxanthine, xanthine, theobromine, and caffeine, when subjected to successive oxidation and reduction under the same conditions as uric acid, also yield murexide, and the absorption of iodine by urine is partly due to the presence of the two first-named compounds. It is found, in fact, that the elimination of the uric acid and urates from urine does not wholly obviate the difficulties in the detection of traces of iodides therein. N. L.

**Nitrobiuret and Amidobiuret.** By JOHANNES THIELE and EMIL UHLFELDER (*Annalen*, 1898, **303**, 93—107).—*Nitrobiuret*,

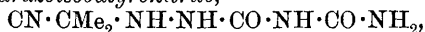


prepared by adding biuret in small portions to a mixture of concentrated nitric and sulphuric acids, separates from water as a white, crystalline powder, which melts and decomposes at  $165^\circ$ ; it does not develop colour with alkali and copper sulphate, but gives the nitramine reaction with ferrous sulphate and sulphuric acid, and is resolved by boiling water into carbonic anhydride, nitrous oxide, and carbamide. The *potassium* and *silver* derivatives are anhydrous.

*Dinitrobiuret*,  $\text{NH}(\text{CO} \cdot \text{NH} \cdot \text{NO}_2)_2$ , produced when the finely divided nitro-derivative is added to fuming nitric acid cooled with a freezing mixture, crystallises from methylic alcohol in white needles, and explodes at  $124^\circ$ ; it gives the nitramine reaction, and is resolved into nitrous oxide, carbonic anhydride, and ammonia under the influence of boiling water. The *potassium* derivative crystallises from water in colourless, rhombic plates.

*Benzylideneamidobiuret*,  $\text{CHPh} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , obtained on reducing nitrobiuret, and treating the product with benzaldehyde, crystallises from alcohol in small, white needles, and melts at  $202^\circ$ . *Amidobiuret hydrochloride* is formed when the benzylidene derivative, moistened with alcohol, is heated with concentrated hydrochloric acid on the water-bath; it crystallises from alcohol in plates, and melts at  $185^\circ$ . It dissolves readily in water, and is gradually resolved into ammonium chloride and hydrazodicarbonimide (urazole) when the aqueous solution is boiled; it reduces cold, ammoniacal silver nitrate and hot Fehling's solution. The *nitrate* crystallises from boiling alcohol in beautiful needles, and melts at  $165^\circ$ ; it is best prepared by the action of concentrated nitric acid on the *acetone* ( $\beta$ -propylidene) compound,  $\text{CMe}_2 \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , which crystallises in white needles and melts at  $189^\circ$ . The *picrate* melts at  $175^\circ$ .

*Allophanylhydrazoisobutyronitrile*,\*



prepared by the action of hydrogen cyanide on the acetone compound of amidobiuret, crystallises in prismatic plates and melts at  $146^\circ$ ; oxidation with potassium permanganate converts it into *allophanylazoisobutyronitrile*,  $\text{CN} \cdot \text{CMe}_2 \cdot \text{N} \cdot \text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , which crystallises from benzene in yellow, rhombic plates, and melts and decomposes at  $127^\circ$ .

*Allophanazide*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{N} < \underset{\text{N}}{\text{N}}$ , obtained by the action of

nitrous acid on amidobiuret, melts and decomposes at  $195^\circ$ ; it is insoluble in water, but dissolves in aqueous ammonia and in alcohol, undergoing decomposition. Silver nitrate precipitates, from the alcoholic solution, a white, highly explosive substance, which dissolves in ammonia and nitric acid. When the azide is heated with boiling alcohol, diazoimide is eliminated, and ethylic allophanate produced.

*Tetruret*,  $\text{NH}(\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2)_2$ , prepared by the action of ammonia on allophanazide, crystallises in colourless, rhombic prisms, and

\* *Allophanyl* is the name given by the authors to the radicle  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO}$ .



melts at  $186^{\circ}$ ; copper sulphate and alkali develop a deep violet coloration, more intense, but less red than the biuret reaction. M. O. F.

**Nitrodicyanodiamidine and Amidodicyanodiamidine.** By JOHANNES THIELE and EMIL UHLFELDER (*Annalen*, 1898, 303, 107—114).—*Nitrodicyanodiamidine*,  $\text{NO}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH}$ , prepared by adding dicyanodiamide to a mixture of concentrated nitric and sulphuric acids, forms a microcrystalline powder soluble with difficulty in water and in alcohol; it is neutral in reaction, and when heated with water, becomes alkaline, with elimination of nitrous oxide and carbonic anhydride, guanidine carbonate crystallising from the liquid. The *silver* derivative decrepitates when heated.

*Amidodicyanodiamidine dihydrochloride* forms white needles and melts at  $191^{\circ}$ ; the *picrate* becomes brown at  $198^{\circ}$ , and melts at  $236^{\circ}$ . The benzylidene compound forms a *hydrochloride*, which crystallises from alcohol in white prisms and melts at  $226^{\circ}$ .

*Acetoneamidodicyanodiamidine hydrochloride*,



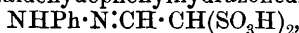
crystallises from alcohol in small, white leaflets and needles, and melts at  $206^{\circ}$ .

*Guanidinecarboxylazide hydrochloride*,  $\text{N}_3 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{HCl}$ , prepared by adding cold, aqueous amidodicyanodiamidine hydrochloride to chloroform saturated with dried nitrous anhydride, melts at  $157^{\circ}$ , and explodes when heated on platinum foil. Boiling alcohol eliminates diazoimide, and yields the compound  $\text{C}_4\text{H}_{10}\text{N}_4\text{O}_5$ , which crystallises in elongated, thin prisms and melts at  $187^{\circ}$ .

M. O. F.

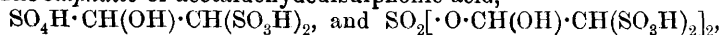
**Chemistry of Acetylene.** By GEORG SCHROETER (*Annalen*, 1898, 303, 114—132. Compare Abstr., 1898, i, 614).—Acetaldehydedisulphonic acid,  $\text{COH} \cdot \text{CH}(\text{SO}_3\text{H})_2$ , produced by the action of concentrated sulphuric acid on acetylene, has not been obtained crystalline, but forms a syrup which dissolves in alcohol. The *barium* salt contains  $2\text{H}_2\text{O}$ , and the *basic barium* salt, which is less readily soluble, crystallises from water in needles containing  $4\text{H}_2\text{O}$ ; the *potassium* salt contains  $1\text{H}_2\text{O}$ , and when treated with potassium hydrogen sulphite, yields the potassium hydrogen sulphite compound of potassium acetaldehydedisulphonate, already obtained by Rathke from chloral and potassium sulphite. The *sodium* salt dissolves in water more freely than the barium and potassium salts, and contains  $1\text{H}_2\text{O}$ ; the *silver*, *copper*, and *lead* salts are also readily soluble, and the *basic lead* salt contains  $1\text{H}_2\text{O}$ .

Acetaldoximedisulphonic acid,  $\text{NOH} \cdot \text{CH} \cdot \text{CH}(\text{SO}_3\text{H})_2$ , forms a *potassium* salt which crystallises from water in lustrous needles containing  $1\text{H}_2\text{O}$ . Acetaldehydophenylhydrazonedisulphonic acid,



forms a *barium* salt which crystallises from water in leaflets containing  $2\text{H}_2\text{O}$ . Acetalazinetetrasulphonic acid,  $\text{N}_2[\text{CH} \cdot \text{CH}(\text{SO}_3\text{H})_2]_2$ , forms a *barium* salt which contains  $6\text{H}_2\text{O}$ ; the *hydrazine* salt contains  $2\text{H}_2\text{O}$ , and decomposes at  $200^{\circ}$ .

The *sulphates* of acetaldehydedisulphonic acid,



are also produced when fuming sulphuric acid is saturated with acetylene. M. O. F.

**1:2-Acetylfurfuran; and its Occurrence in Wood Tar.** By LOUIS BOUVEAULT (*Compt. rend.*, 1897, 125, 1184—1186).—This compound is produced synthetically by heating together on the water-bath ethylic pyromucate and ethylic acetate in the presence of sodium. The product, after treatment with dilute hydrochloric acid, yields 1:2-ethylic pyromucylacetate,  $C_4OH_3 \cdot CO \cdot CH_3 \cdot COOEt$ , which boils at 142—143° under a pressure of 10 mm. and has an odour resembling that of ethylic acetoacetate.

2-Acetylfurfuran,  $\begin{matrix} CH:CH \\ CH:CAc \end{matrix} > O$ , produced by the hydrolysis of the preceding compound with 25 per cent. sulphuric acid, boils at 67° under a pressure of 10 mm., solidifies to a mass of crystals melting at 29.5°, and has an odour recalling that of acetophenone.

The oil boiling between 150—200°, obtained by the distillation of beech- and oak-wood after removal of the phenolic and basic substances, is rectified under reduced pressure. The fraction boiling between 60° and 70° under a pressure of 10 mm. is treated with excess of hydroxylamine; the product distilled under the same pressure yields a mixture of oximes boiling at 105—115°. The distillate yields a crop of crystals melting at 127—128°, and consisting of the oxime of methyleyclopentenone,  $C_6H_8O$ , a compound already obtained from wood tar. By warming the oxime with acetic anhydride, an acetyl derivative,  $C_6H_8N \cdot OAc$ , is produced, which boils at 123° under a pressure of 10 mm., and crystallises in needles melting at 73°.

The greater portion of the rectified oximes remains liquid, and on treatment with acetic anhydride yields the acetyl derivative of 1:2-acetylfurfuranoxime which boils at 135° under a pressure of 10 mm., and crystallises from ether in needles melting at 96°. 1:2-Acetylfurfuranoxime is obtained by hydrolysing the acetyl compound with alcoholic potash; it boils at 110—111° under a pressure of 10 mm., and crystallises from ether in well-defined prisms melting at 104°.

When the oxime is hydrolysed with 25 per cent. sulphuric acid, 1:2-acetylfurfuran is regenerated. G. T. M.

**Decomposition of Pyromucates of the Alkaline Earths.** By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 609—612).—The author has prepared furfuran by Limpricht's method (*Annalen*, 1873, 165, 281), namely, by heating barium pyromucate with soda-lime. It is not advisable to use more than 100 grams of the barium salt at once, and the yield is extremely poor, only some 4—6 grams of furfuran being obtained from 100 of the barium salt. A considerable amount of gas is evolved during the reaction, and this consists of equal volumes of an unsaturated hydrocarbon,  $C_3H_4$  (this vol., i, 98), and of carbonic oxide, or hydrogen when an excess of soda-lime is employed. No better yield could be obtained by employing the calcium in place of the barium salt. Experiments have also been made by heating the barium salt with barium oxide under reduced pressure, and also by

heating the barium salt alone, both under atmospheric and reduced pressures; the products obtained in all cases were furfuran (10—12 per cent., hydrocarbon,  $C_3H_4$  (5—6 per cent.), carbonic oxide (3—4 per cent.), hydrogen and the ketone,  $(C_4H_3O)_2CO$  (1—2 per cent.).

J. J. S.

**A New Series of Cyclic Ketones.** By AUGUSTE BÉHAL (*Compt. rend.*, 1897, 125, 1036—1038).—The heavy oil obtained by the distillation of wood tar consists of a mixture of acidic, basic, and neutral substances; the new ketones are separated from the neutral portions by extraction with concentrated hydrochloric acid, in which they are soluble. The acidic extract, diluted, and subjected to distillation with steam, yields a distillate containing the ketones in the form of a supernatant, yellow oil having an odour of menthol, and boiling between  $180^\circ$  and  $205^\circ$ .

The ketones differ in their solubility in hydrochloric acid, and a partial separation may be effected by the use of various strengths of acid. The greater portion of the mixture is dissolved by a solution of dilute acid (1 : 2), and this portion, when rectified, distils at  $190^\circ$ — $192^\circ$ . The ketones in the distillate are converted into oximes, and these into their benzoyl derivatives. The latter can be separated into two distinct substances, the one less soluble in benzene, alcohol, and ether, and melting at  $167^\circ$ , the other far more soluble in these solvents and melting at  $128^\circ$ — $129^\circ$ . The oximes are regenerated by the alkaline hydrolysis of the two benzoyl derivatives, that derived from the less soluble benzoyl derivative (m. p.  $167^\circ$ ) melting at  $121.5^\circ$ , and that from the more soluble compound (m. p.  $129^\circ$ ) at  $102.5^\circ$ .

The parent ketones are obtained by distilling the oximes with 20 per cent. hydrochloric acid. The oxime of higher melting point yields a ketone which boils at  $192^\circ$  under a pressure of 760 mm., and is soluble in water and the ordinary organic solvents. This ketone can be obtained in crystals and melts at  $12^\circ$ ; its sp. gr. = 0.9866 at  $0^\circ$ .

Another ketone, which also boils at  $192^\circ$ , is furnished by the oxime of lower melting point; it does not solidify when cooled to  $-27^\circ$ ; it is soluble in water and the ordinary organic solvents, and its sp. gr. = 0.9539 at  $0^\circ$ .

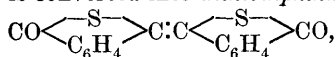
The quantity of these ketones in the heavy oil of wood tar amounts to 16 per cent., and they belong chiefly to the tetrahydrobenzene series.

G. T. M.

**Action of Potassium Hydrosulphide on Orthocyanobenzyl chloride.** By SIEGMUND GABRIEL and ERNST LEUPOLD (*Ber.*, 1898, 31, 2646—2654. Compare *Abstr.*, 1890, 1249).—When orthocyanobenzyl chloride is treated with potassium hydrosulphide, a compound,  $C_6H_7NS$ , is produced, which may be regarded either as orthocyanobenzyl mercaptan,  $CN \cdot C_6H_4 \cdot CH_2 \cdot SH$ , or as thiophthalimidine,  $C_6H_4 \langle \begin{smallmatrix} CH_2 \\ C(NH) \end{smallmatrix} \rangle S$ . The continued action of potassium hydrosulphide

produces *dithiophthalide*,  $C_6H_4 \langle \begin{smallmatrix} CH_2 \\ CS \end{smallmatrix} \rangle S$ , which crystallises in reddish, flat plates melting at  $68^\circ$ ; this substance again is converted by excess of the sulphide into a sparingly soluble compound,  $C_{16}H_{10}S_3$ , which

crystallises in needles with a green reflex, and probably has the constitution  $\text{CH}_2\langle\text{C}_6\text{H}_4\text{S}\rangle\text{C}:\text{C}\langle\text{C}_6\text{H}_4\text{S}\rangle\text{CS}$ . On oxidation with nitric acid, this compound is converted into *dithiodiphthalyl*,



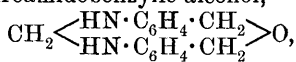
which crystallises in long, greenish-yellow needles, and melts at  $332-333^\circ$  (uncorr.). Fuming nitric acid converts dithiodiphthalyl into diphthalyllic acid,  $\text{C}_{16}\text{H}_{10}\text{O}_6$ , and its constitution is thus established. When this is boiled with alkalis, it yields a salt of the corresponding hydroxy-acid, which is decomposed by acids, with formation of the dilactone. When a solution of dithiodiphthalyl in alcoholic sodium methoxide is treated with methyl iodide, the *tetramethylic* derivative  $\text{SMe}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})\cdot\text{C}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{SMe}$ , of this acid is produced, which crystallises in yellow, six-sided tablets melting at  $160-161^\circ$ ; on reduction, this methylic derivative is converted into two isomeric compounds,  $\text{C}_{16}\text{H}_{10}\text{O}_4$ , one of which is an acid, and the other an indifferent substance. The former crystallises in oblique prisms and melts at  $228-229^\circ$ , whilst the latter forms snow-white needles melting at  $255-257^\circ$ ; the constitution of these two compounds is shown by the fact that they are both formed when deoxybenzoinorthodicarboxylic acid,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , is heated, and are reconverted into this acid when they are heated with alkalis. The indifferent substance is, therefore, an inner anhydride of deoxybenzoindicarboxylic acid, whilst the acid is a lactonic acid, the exact constitution being still uncertain in both cases.

A. H.

**Electrolytic Reduction of the Nitro-group.** By WALTHER LÖB (*Zeit. Elektrochem.*, 1898, 4, 428. Compare Abstr., 1897, i, 331; and 1898, i, 14).—The author's object was to isolate intermediate reduction products by adding a substance which will combine with them, and so withdraw them from further reduction. When a mixture of 10 grams of nitrobenzene, 35 grams of fuming hydrochloric acid, 25 c.c. of water, and 70 c.c. of alcohol is placed in a porous cell containing a lead cathode, and this is immersed in dilute sulphuric acid (1 : 10) containing a platinum anode, aniline is practically the only product obtained with E.M.F.'s from 2.5 to 6 volts, and temperature from  $20^\circ$  to  $80^\circ$ . When the 25 c.c. of water is replaced by 25 c.c. of 40 per cent. formaldehyde solution, and the electrolysis conducted with 5 volts and 2 ampères, at  $45-60^\circ$ , a polymeride of paranhydroxyhydroxylaminobenzyl alcohol,  $(\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH} - \text{H}_2\text{O})_n$ , is obtained. This compound is also formed by the interaction of phenylhydroxylamine and formaldehyde in presence of hydrochloric acid. It is a red, amorphous powder, which yields paraleucaniline with aniline and aniline hydrochloride, whilst with nitrous acid a diazo-derivative is formed which yields parahydroxybenzaldehyde on boiling. Its hydrochloride dissolves in warm, concentrated hydrochloric acid, and the free base is obtained by pouring this solution into dilute ammonia. The base decomposes at high temperatures without melting, may be boiled with caustic soda without decomposition, is insoluble in most

solvents, slightly soluble in chloroform, and more so in aniline and concentrated sulphuric acid.

When the electrolysis is carried out with 2·8—3 volts at 30°, methylenediparanhydroamidobenzyl alcohol,



is the only product. This substance has not previously been described, and may be obtained by the direct interaction of aniline and formaldehyde. The hydrochloride and platinochloride were analysed. The base is a pale yellow, amorphous powder, soluble in dilute acids, chloroform, and aniline, less soluble in alcohol and glacial acetic acid, insoluble in water, ether, alkalis, and light petroleum. Its solutions in acids are yellow or red.

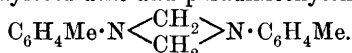
When nitrobenzene (10 grams), 40 per cent. formaldehyde (10 grams), alcohol (10 grams), and fuming hydrochloric acid (35 grams) are gradually treated with zinc dust (20 grams) at 50°, paranhydroxylaminobenzyl alcohol is formed almost quantitatively.

In order to prevent the reaction of the formaldehyde with the hydrogen atom in the para-position to the nitro-group, experiments were tried with paranitrotoluene.

Paranitrotoluene (10 grams), alcohol (100 c.c.), water (4 c.c.), and sodium hydroxide (5 grams) were electrolysed as above described with 1·3 ampères and 5—6 volts. A quantitative yield of parazotoluene was obtained.

Paranitrotoluene (10 grams), suspended in fuming hydrochloric acid (100 c.c.), and electrolysed with 5 volts and 1·7 ampères, gave a quantitative yield of paratoluidine.

Paranitrotoluene (10 grams), alcohol (80 c.c.), water (35 c.c.), and fuming hydrochloric acid (35 grams) electrolysed with 1·5 ampères and 4 volts, also gave an almost quantitative yield of paratoluidine. In the last case, when the water was replaced by 40 per cent. formaldehyde, two substances were obtained in nearly equal quantities, namely, paradimethyltoluidine and paradimethyleneditoluidine,



The latter is formed almost quantitatively by the action of formaldehyde on paratoluidine in acid solution, and crystallises from dilute alcohol in slender needles melting at from 119—125°; it cannot be reduced, either chemically or electrolytically, to paradimethyltoluidine, except in presence of formaldehyde, when the reduction proceeds perfectly smoothly, yielding paradimethyltoluidine and paratoluidine.

T. E.

**Reduction of 2-Nitro-3:5-dimethylphenylnitromethane [ $\omega$ -2-Dinitromesitylene].** By EUGEN BAMBERGER and MAX WEILER (*J. pr. Chem.*, 1898, [ii], 58, 333—361).—When  $\omega$ -2-dinitromesitylene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH}_2 \cdot \text{NO}_2$  (Konowaloff, *Abstr.*, 1896, i, 674), is dissolved in 95 per cent. alcohol, and reduced with 4 per cent. sodium amalgam at  $-10^\circ$ , 2-amido-3:5-dimethylbenzaloxime,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH} \cdot \text{NOH}$ , is formed; this melts at 170—171°, dissolves in dilute mineral acids and caustic alkalis, forms a *dibenzoyl* derivative melting at 142—142·5°,

and a yellow compound melting at 179—180°, when mixed with meta-nitrobenzaldehyde in dilute hydrochloric acid solution. When boiled with dilute sulphuric acid, it yields 1-amido-3:5-dimethylbenzaldehyde,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CHO}$ , identical with a product obtained from mesitylene in the manner described below; this is yellow, and melts at 48—49°; with phenylhydrazine, it yields a substance melting at 142—143°, and possibly not a normal hydrazone, as it is not soluble in acids. When the oxime is boiled for a short time with acetic anhydride, it forms 2-acetamidomesitylenonitrile,  $\text{NHAc} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CN}$ , together with a substance that melts at about 150°; the nitrile melts at 196·5—197·5°, and is insoluble in dilute acids and alkalis, but when warmed with these it is converted into a substance that melts at 271·5—272·5°; the latter has the properties of a quinazolone (Weddigé, Abstr., 1885, 661; 1887, 1044), and must, therefore, be trimethylquinazolone,

$\text{C}_6\text{H}_2\text{Me}_2 \cdot \begin{matrix} \text{CO} \cdot \text{NH} \\ | \\ \text{N} = \text{C} \end{matrix} \text{Me}$ ; its orange-yellow platinochloride is still un-

melted at 345°. When the oxime is dissolved in a mixture of acetic acid and anhydride, and the mixture is saturated with gaseous hydrogen chloride at 0° and allowed to remain (Beckmann's mixture), the product, which melts at 166·5—168°, has the properties of an acetylindazole (Auwers, Abstr., 1892, 186; 1896, i, 504), and consequently must be acetyldimethylindazole,  $\text{C}_6\text{H}_2\text{Me}_2 \cdot \begin{matrix} \text{CH} \\ \diagup \diagdown \\ \text{N} \text{---} \text{Ac} \end{matrix}$ ; it is

soluble in cold, dilute hydrochloric acid, but not in cold, aqueous caustic potash; when boiled with the latter, it dissolves gradually, and from the solution acetic acid precipitates a substance melting at 191·5—192·5°, which possibly may be 2-acetamido-3:5-dimethylbenzaldoxime. When the amidodimethylbenzaldoxime is diazotised in hydrochloric acid solution with sodium nitrite, the product is

dimethylindiazone oxime,  $\text{C}_6\text{H}_2\text{Me}_2 \cdot \begin{matrix} \text{C}(\text{NOH}) \\ \diagup \diagdown \\ \text{N} \end{matrix} \text{N}$ ; this is yellow, melts

and decomposes at 181·5—182·5°, and dissolves in cold, dilute mineral acids and alkalis, but is decomposed by these on boiling, the products being, when acid is used, hydroxylamine; amidodimethylbenzaldehyde (see above); dimethylsalicylaldehyde, which solidifies at about 15°, and forms an oxime,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CH} \cdot \text{NOH}$ , melting at 138·5—139·5°; and a substance which forms an oxime melting at 99—100·5° and is devoid of acid character.

If  $\omega$ -2-dinitromesitylene is dissolved in commercial absolute alcohol and reduced with 4 per cent. sodium amalgam at -5° to 0°, the products then obtained are a resin; mesitylenic acid; amidodimethylbenzaldoxime; a base,  $(\text{C}_9\text{H}_{12}\text{NO})_x$ , possibly  $\text{C}_2\text{H}_2(\text{OH})_2(\text{C}_6\text{H}_2\text{Me}_2 \cdot \text{NH}_2)_2$ , which melts at 260°; another base, or mixture of bases, which melts at 133—147·5°, and has the composition C, 70·2—72·0; H, 8·26—8·51; N, 9·15 (these last two bases are insoluble in alkalis); and a small quantity of an acid containing nitrogen.

2-Amido-3:5-dimethylbenzaldehyde was prepared from mesitylene by oxidising it to bimethylbenzaldehyde with chromyl chloride in carbon bisulphide solution; or, better, by converting it into mesitylic bromide and oxidising this with chromate or lead nitrate, nitrating the aldehyde with a solution of potassium nitrate in strong sulphuric

acid cooled by a freezing mixture, and reducing the 2-nitro-3:5-dimethylbenzaldehyde,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}_2 \cdot \text{CHO}$ , which melts at  $102-103^\circ$ , with ferrous sulphate and ammonia. C. F. B.

**Hydrolysis of Ethanedicatchol [Dicatchol Acetylenic Ether].** By CHARLES MOUREU (*Compt. rend.*, 1898, 127, 276—278).—The compound  $\text{C}_8\text{H}_8\text{O}_4$ , obtained by boiling dicatchol acetylenic ether with dilute sulphuric acid, is *orthohydroxyphenoxyacetic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ . It is acid to litmus, phenolphthalein, methyl-orange, and the blue—C4B, gives an intense blue coloration with ferric chloride, and reduces ammoniacal silver nitrate in the cold, but gives no coloration with rosaniline hydrogen sulphite. Its phenylhydrazone crystallises in white, rectangular scales which melt and decompose at  $193^\circ$ . When heated, it forms a lactone which crystallises in large, elongated prisms melting at  $54-56^\circ$ , and when boiled with water is reconverted into the acid melting at  $130-131^\circ$ .

The same acid is obtained by heating sodium monochloracetate with monosodium catechol and treating the product with hydrochloric acid.

It is probable that when the dicatchol acetylenic ether is boiled with the dilute acid, the first product is a compound,  $\text{C}_6\text{H}_4 \cdot \text{O}_2 \cdot \text{CH} \cdot \text{CHO}$ , which, by hydration, is converted into  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$ , and the latter, being unstable, changes by intramolecular migration of an oxygen atom into the acid  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ . C. H. B.

**Preparation of Paraquinones from Indophenols.** By PIERRE H. BAYRAC (*Ann. Chim. Phys.*, 1897, [vii], 10, 18—79).—This paper gives full details of work which has already been published (see Abstr., 1895, i, 412, 416; 1896, i, 605, 606). G. T. M.

**Formation of Chains. XXVII. Benzylaniline. XXVIII. Diphenylamine.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 2672—2677, 2678—2683. Compare Abstr., 1898, i, 182).—Chain formation occurs less readily in the case of benzylaniline and of diphenylamine than with the secondary bases discussed in the preceding papers; this is indicated by the numbers in the following table, which give the approximate extent in percentages of the theoretical maximum to which action takes place between the amines and ethylic salts there tabulated.

Ethylic salt.	Benzylaniline.			Diphenylamine.				
	At 100°.	At 110°.	At 120°.	At 100°.	At 110°.	At 120°.	At 170—175°.	At 195—200°.
Bromopropionate...	Nil	29.2	50.9		Nil	36.1	33.5	55.8
Bromophenyl- acetate .....	40.3			27.0			42.0	
Bromobutyrate .....			14.0			4.4	8.3	
Bromisobutyrate ...			Nil			9.1		
Bromisovalerate ...			Nil			3.0		

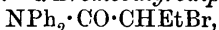
The following new substances were prepared in the course of the investigation.

*Phenylbenzylglycine*,  $\text{CH}_2\text{Ph} \cdot \text{NPh} \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared from

benzylaniline, chloracetic acid, and sodium acetate, crystallises from alcohol in needles, and melts at 121—123°; it decomposes on exposure to light and air, when an intense odour of benzaldehyde becomes perceptible.

*α-Bromopropionobenzylanilide*,  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CHMeBr}$ , formed by the action of *α*-bromopropionic bromide on benzylaniline, separates from alcohol in crystals belonging to the rhombic system and melts at 78°. *α-Bromobutyrobenzylanilide*,  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CHEtBr}$ , is deposited by dilute alcohol in colourless crystals and melts at 50—54°; *α-bromisobutyrobenzylanilide*,  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$ , is an oil. *α-Bromisovalerobenzylanilide*,  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHMe}_2$ , crystallises from 96 per cent. alcohol in aggregates of colourless prisms and melts at 95—96°.

*α-Bromopropionodiphenylamide*,  $\text{NPh}_2\cdot\text{CO}\cdot\text{CHMeBr}$ , separates from hot alcohol in colourless, transparent crystals belonging to the monoclinic system and melts at 109°. *α-Bromobutyrodiphenylamide*,



is deposited by alcohol in large, lustrous crystals and melts at 85°. *α-Bromisobutyrodiphenylamide*,  $\text{NPh}_2\cdot\text{CO}\cdot\text{CMe}_2\text{Br}$ , crystallises from alcohol in plates, and melts at 82°. *α-Bromisovalerodiphenylamide*,  $\text{NPh}_2\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHMe}_2$ , crystallises in colourless, four-sided plates, and melts at 110·5°. M. O. F.

**Peracetylation of Phenacetine.** By AUGUSTIN BISTRZYCKI and FRITZ ULFFERS (*Ber.*, 1898, 31, 2788—2790. Compare *Abstr.*, 1894, i, 181, and Kay, *ibid.*, 77).—Phenacetine,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , is boiled for several hours with a large excess of acetic anhydride in a reflux apparatus, moisture being excluded by means of a calcium chloride tube; the acetic acid formed and some of the anhydride is distilled over; the residue is boiled again with more acetic anhydride, the product distilled under 15 mm. pressure in an oil bath at 180°, and the residue poured out. In this way, *diacetophenetidine*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NAc}_2$ , is obtained; it melts at 53·5—54°, and boils at 182° under a pressure of 12 mm.; when kept in stoppered bottles, it is decomposed very slowly by the moisture of the air, acetic acid being formed; its physiological action is similar to that of phenacetine, and the same effect is sometimes obtained, although it is commonly less lasting, with a smaller dose, than in the case of phenacetine.

C. F. B.

**Potassiodiphenylamine.** By CARL HÄUSSERMANN (*J. pr. Chem.*, 1898, [ii], 58, 367—368).—Diphenylamine (30 parts) is melted in a strong, round-bottomed flask in a boiling water-bath, potassium (1 part) is added little by little, and as soon as the violent action has ceased, the flask is exhausted of air and the heating is continued for 3—4 hours until the potassium has disappeared, after which unchanged diphenylamine is removed by digestion with absolute ether. The product, presumably  $\text{NPh}_2\text{K}$ , is a yellow, sandy powder, which absorbs oxygen from the air, turning black, and unites with dry carbonic anhydride to form *potassium diphenylthiocarbamate*,  $\text{NPh}_2\cdot\text{COOK}$ , a white powder which is decomposed by water into diphenylamine and potassium hydrogen carbonate. C. F. B.



**Nitroso-derivatives of Aromatic Amines.** By CAMILLE MATIGNON and DELIGNY (*Compt. rend.*, 1897, 125, 1103—1105).—The authors have made a comparative study of the heats of combustion of the following nitroso-compounds of aromatic amines: diphenylnitrosamine, nitrosophenylaniline, and paranitrosodimethylaniline. They find that the introduction of a nitroso-group into the aromatic nucleus lowers the heat of combustion by 15 calories, whereas its attachment to the nitrogen of the side-chain lowers this by 9·8 calories. This difference explains the readiness with which the nitroso-group migrates from the nitrogen atom into the nucleus. Provided that the molecules originally contain a sufficient number of atoms, the introduction of a new radicle produces the same change in the heats of combustion if the entering group becomes similarly attached in each case. G. T. M.

**Behaviour of Substituted Amidonitriles towards Aromatic Aldehydes in Presence of Alkali.** By WILHELM VON MILLER and JOSEF PLÖCHL (*Ber.*, 1898, 31, 2699—2717).—Substituted amidonitriles yield alkylideneamides with aromatic aldehydes, just as they give rise to amides under the influence of water.

[With BR. BRUHN.]—The compound  $C_{21}H_{18}N_2O$ , obtained by the action of benzaldehyde on benzylideneaniline under the influence of alcoholic potassium cyanide, is also produced gradually in absence of benzaldehyde; it crystallises from amyl alcohol or nitrobenzene in microscopic needles and melts at  $249^\circ$ . The *isomeride*, formed at the same time, crystallises from alcohol in pale yellow prisms melting at  $208^\circ$ ; it is accompanied by a small quantity of a substance which crystallises in pink leaflets and melts at  $151^\circ$ . The compound  $C_{23}H_{20}N_2O_3$  is also produced; it melts and decomposes at  $194^\circ$  and is distinctly acidic in character. The three compounds are formed when alcoholic potassium cyanide acts on the nitrile of phenylanilidoacetic acid and benzaldehyde, and they are all resolved into benzaldehyde, ammonia, and phenylanilidoacetic acid under the influence of boiling dilute hydrochloric acid. The less readily fusible isomeride is converted into that melting at  $208^\circ$  by the action of boiling alcoholic potash, and of boiling glacial acetic acid; the action in each case is reversible.

[With LUDWIG GERNGROSS.]—From phenylanilidoacetonitrile and cuminaldehyde dissolved in alcoholic potash, two indifferent, isomeric compounds,  $C_{24}H_{24}N_2O$ , are obtained melting at  $226^\circ$  and  $198^\circ$  respectively; they are also produced by the action of cuminaldehyde on benzylideneaniline, along with an acidic compound,  $C_{25}H_{26}N_2O_3$ , and the nitrile,  $C_{25}H_{25}N_3O$ , which melt at  $208^\circ$  and  $256^\circ$  respectively. The indifferent compounds are interconvertible, and, like the acid, yield cuminaldehyde, ammonia, and phenylanilidoacetic acid with boiling hydrochloric acid; phenylhydrazine gives rise to cuminalphenylhydrazone.

*Cumenylanilidoacetonitrile*,  $C_{17}H_{18}N_2$ , from cumylideneaniline and hydrogen cyanide, crystallises from alcohol in lustrous, monoclinic prisms and melts at  $86^\circ$ . *Cumenylanilidoacetamide*,  $C_{17}H_{20}N_2O$ , obtained by the action of concentrated sulphuric acid on the nitrile, forms colourless prisms melting at  $159^\circ$ , and yields a *nitroso-deriva-*

tive which melts at  $132^{\circ}$ . *Cumenylanilidoacetic acid*,  $C_{17}H_{19}NO_2$ , crystallises in small aggregates of needles; it melts and decomposes at  $158^{\circ}$ .

[With P. SCHEITZ.]—*Benzylideneparanisidine*,  $C_{14}H_{13}NO$ , crystallises in leaflets and melts at  $72^{\circ}$ ; hydrogen cyanide converts it into the *nitrile* of phenylparanisidoacetic acid, which melts at  $85^{\circ}$ , whilst the *amide* melts at  $120^{\circ}$ . *Phenylparanisidoacetic acid*,  $C_{15}H_{15}NO_3$ , melts and decomposes at  $184^{\circ}$ . The two indifferent compounds,  $C_{22}H_{20}N_2O_2$ , obtained from the nitrile with benzaldehyde and alcoholic potash, melt at  $222^{\circ}$  and  $193^{\circ}$  respectively; the acidic compound,  $C_{23}H_{22}N_2O_4$ , melts at  $198^{\circ}$ , with effervescence, and the corresponding *nitrile*,  $C_{23}H_{21}N_3O_2$ , melts at  $233^{\circ}$ .

[With R. LUPPE.]—Anhydroformaldehydeaniline with benzaldehyde and potassium cyanide, or anilidoacetoneitrile with benzaldehyde and alcoholic potash, yields two indifferent compounds,  $C_{15}H_{14}N_2O$ , melting at  $219^{\circ}$  and  $169^{\circ}$  respectively, along with an acidic compound,  $C_{16}H_{16}N_2O_3$ , which melts and effervesces at  $239^{\circ}$ ; when the compound melting at  $169^{\circ}$  is recrystallised from alcohol, it is in part converted into the isomeride, the change being complete on exposing the substance to a temperature of  $170^{\circ}$  during some hours. Boiling 20 per cent. hydrochloric acid resolves the substance into benzaldehyde, ammonia, and anilidoacetic acid.

[With WILHELM SIEBER.]—The indifferent compounds,  $C_{16}H_{16}N_2O$ , obtained from anhydroformaldehydeparatoluidine with benzaldehyde and potassium cyanide, melt at  $245^{\circ}$  and  $168^{\circ}$  respectively; the acidic compound,  $C_{17}H_{18}N_2O_3$ , melts at  $228^{\circ}$ . *Paratoluidoacetic acid*,  $C_6H_4Me \cdot NH \cdot CH_2 \cdot COOH$ , obtained by hydrolysing with 20 per cent. hydrochloric acid the compound which melts at  $245^{\circ}$ , crystallises from light petroleum in large, lustrous, monoclinic plates, and melts at  $132^{\circ}$  (compare Bischoff and Hausdörfer, Abstr., 1892, 1335); the *nitrile* melts and decomposes at  $61^{\circ}$ , and the *amide*, which melts at  $168^{\circ}$ , yields a *nitroso*-derivative melting at  $158^{\circ}$ .

[With J. HAMBURGER.]—Ethylideneaniline, with benzaldehyde and potassium cyanide, yields an indifferent compound,  $C_{16}H_{16}N_2O$ , which melts at  $203^{\circ}$ , and an acidic compound,  $C_{17}H_{18}N_2O_3$ , melting at  $220^{\circ}$ .

[With W. KOLLEGORSKY.]—Benzylidenemethylamine, with benzaldehyde and potassium cyanide, yields an indifferent compound,  $C_{16}H_{16}N_2O$ , which melts at  $152^{\circ}$ , and an acidic compound,  $C_{17}H_{18}N_2O_3$ , melting at  $179^{\circ}$ . Hydrolysis resolves these substances into benzaldehyde, ammonia, and phenylsarcosine.

M. O. F.

**Stereochemistry of Quinoneoximes.** By FRIEDRICH KEHRMANN (*Annalen*, 1898, 303, 1—33. Compare Abstr., 1894, i, 460).—The two modifications in which both the benzoyl and methyl derivatives of metachloroquinoneoxime are produced have been regarded by the author (*loc. cit.*) as stereoisomerides; further evidence in support of this view has been derived from a determination of the molecular weight of the two isomeric acetyl derivatives, and from an examination of the behaviour of parachlorotoluquinone towards hydroxylamine hydrochloride. It being exceptional for the meta-halogen derivatives of toluquinone to yield isomeric oximes, the author concludes that it

is only in the case of a slight difference in the stability of the two forms that the phenomenon is noticeable; when the difference is great, one form only is produced.

[With HUGO GRAB.]—The stable modification of the *acetyl* derivative of metachloroquinoneoxime crystallises from benzene in amber-coloured, four-sided prisms, and melts at 166—167°; the labile *compound* dissolves more readily in benzene, from which it crystallises in yellow leaflets, and melts at 136—137°. Both forms give normal figures for the molecular weight in glacial acetic acid, and yield 4:6:2-chlorodinitrophenol and 6:4-chloramidophenol on oxidation with nitric acid, and on reduction with stannous chloride and hydrochloric acid respectively. The isomerism consequently meets with explanation on the hypothesis of Hantzsch and Werner.

When metachloroquinoneoxime is heated with alcoholic hydroxylamine hydrochloride in a reflux apparatus, it yields metachloroquinonedioxime; the *diacetyl* derivative of this substance occurs only in one modification, which crystallises from benzene in colourless prisms and melts at 171—172°. Oxidation and reduction of the dioxime lead to 1:3:6-chlorodinitrobenzene and 2:1:4-chlorodiamidobenzene respectively.

*Paradichloroquinoneoxime*,  $C_6H_3Cl_2NO_2$ , separates from benzene in two crystalline forms, and melts indefinitely at 155—160°; it is uncertain whether the difference in crystalline structure represents stereoisomerism. The *acetyl* derivative crystallises from benzene in amber-coloured prisms, and melts at 149°.

[With MICH. TICHVINSKY.]—The *oxime* of 4-chlorotoluquinone occurs in two modifications, which are separated by a method described in the original paper. The more sparingly soluble isomeride crystallises from alcohol in lustrous, brownish-yellow prisms, and decomposes at 170°; the *acetyl* derivative melts at 158—159°. The more readily soluble modification crystallises from alcohol and from toluene in aggregates of slender, pale yellow needles, and decomposes at about 165°; the *acetyl* derivative crystallises in long needles from the benzene mother liquor of the isomeride, and melts at 141—142°.

*Chloramidocresol* [ $Me:NH_2:Cl:OH = 1:2:4:5$ ], obtained by reducing either modification of the oxime with stannous chloride and hydrochloric acid, forms colourless leaflets and melts at 204—205°; the *diacetyl* derivative crystallises from benzene in colourless needles and melts at 162°.

*Chlorodinitrocresol* [ $Me:(NO_2)_2:Cl:OH = 1:2:6:4:5$ ], produced by the action of dilute nitric acid on either modification of the oxime, crystallises from alcohol in yellow leaflets and melts at 108°.

[With CARL RÜST.]—4-Bromotoluquinone [ $Me:O_2:Br = 1:2:5:4$ ], prepared by treating toluquinone with fuming hydrogen bromide and oxidation of the product with chromic acid, crystallises from alcohol in large, yellow plates and melts at 105°. The *oxime* occurs in two modifications, the more sparingly soluble forming brownish-yellow needles which decompose at 186°, whilst the more readily soluble crystallises from toluene in slender, pale yellow needles and decomposes at 178—180°; the *acetyl* derivatives melt at 166—167° and 131—132° respectively. The corresponding *benzylic ethers* melt at

95—96° and 80—81° respectively; the latter crystallises in the asymmetric system, and has the axial ratio  $a : b : c = 1.7562 : 1 : 1.1580$ .

*Bromamidometacresol* [ $\text{Me} : \text{NH}_2 : \text{Br} : \text{OH} = 1 : 2 : 4 : 5$ ], prepared by reducing either oxime, forms silvery leaflets, and decomposes at 205—208°; the *diacetyl* derivative crystallises from toluene in colourless prisms and melts at 171—172°.

*Bromodinitrometacresol* [ $\text{Me} : (\text{NO}_2)_2 : \text{Br} : \text{OH} = 1 : 2 : 6 : 4 : 5$ ], obtained from both modifications of the oxime by the action of moderately concentrated nitric acid on the water-bath, crystallises from petroleum in sulphur-yellow octahedra and melts at 115—116°; trinitrocresol, which melts at 106—107°, is produced along with it.

M. O. F.

**Ethers of Toluquinoneoxime and their Bearing on the Space-isomerism of Nitrogen.** By JOHN L. BRIDGE and WILLIAM C. MORGAN (*Amer. Chem. J.*, 1898, 20, 761—776).—Toluquinoneorthoxime, which is readily prepared by the action of nitrous acid on metacresol, melts at 155°, not at 145—150°, as stated by Beilstein; toluquinonemetoxime, prepared similarly from orthocresol, melts at 134°. The *silver* derivative,  $\text{C}_7\text{H}_6\text{NO}_2\text{Ag}$ , of the metoxime, when freshly prepared, is a light reddish-brown powder, which slowly decomposes on exposure to the air, and when thoroughly dry ignites spontaneously on being heated above 60°; when shaken with methylic iodide dissolved in light petroleum, it is partially converted into the corresponding *methyl* derivative,  $\text{C}_8\text{H}_9\text{NO}_2$ ; this can be better obtained, however, by adding the calculated quantity of methoxylamine hydrochloride to toluquinone dissolved in a large quantity of water. The product in either case, after being recrystallised several times from light petroleum, melts indefinitely between 55° and 70°, and appears to consist of a mixture of two stereoisomerides; one more sparingly soluble in light petroleum, can be isolated by fractional crystallisation and melts at 73—74°, but the second modification cannot be separated. The corresponding *acetyl* derivative,  $\text{C}_9\text{H}_9\text{NO}_3$ , formed in small quantity on adding acetic chloride to the silver derivative suspended in ether or light petroleum, is resolved by fractional crystallisation from the latter into two stereoisomerides; one of these melts at 112—113°, and crystallises in thick prisms, whilst the other forms spherical aggregates of minute crystals and melts at 85—87°. The *benzoyl* derivative,  $\text{C}_{14}\text{H}_{11}\text{NO}_3$ , prepared by acting on the sodium salt of toluquinonemetoxime prepared from orthocresol, is identical with that obtained from the oxime prepared from toluquinone and hydroxylamine hydrochloride; both products are mixtures of two stereoisomerides, one crystallising in bright yellow needles and melting at 193°, the other separating in thick prisms, and melting probably at 142—144°, although fractions were obtained melting at 129°. No trace of the orthoxime could be detected in the product obtained from toluquinone. On adding bromine to a chloroform solution of the benzoate of the metoxime, the *dibromide*,  $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{NO}_3$ , is obtained; it crystallises from glacial acetic acid in white prisms, melts and decomposes at 165°, and is converted by boiling alcohol into a mixture of two stereoisomeric *benzoates*,  $\text{C}_{14}\text{H}_{10}\text{BrNO}_3$ , of bromotoluquinonemetoxime; the crude

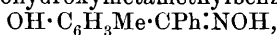
product melts and decomposes at 155—170°, but after fractional crystallisation from alcohol melts and decomposes at 174°.

The *silver* derivative,  $C_7H_6NO_2Ag$ , of toluquinoneorthoxime closely resembles the corresponding meta-derivative, but is much more stable than the latter. The *methyl* derivative,  $C_8H_5NO_2$ , obtained from it crystallises from light petroleum in long needles, melts at 69°, and appears to exist only in one form; when the calculated quantity of bromine is added to its solution in chloroform, the *dibromide*,  $C_8H_5Br_2NO_2$ , is obtained which crystallises from light petroleum in white prisms and melts at 112°. The same acetyl derivative as was prepared by Wurster and Riedel (Abstr., 1880, 109) from acetic anhydride and toluquinoneorthoxime is formed in small quantity by acting on the silver derivative of the latter with acetic chloride. The corresponding *benzoyl* derivative,  $C_{14}H_{11}NO_3$ , crystallises from alcohol in flat, brownish-yellow prisms, and melts and partially decomposes at 177°; the *dibromide*,  $C_{14}H_{11}Br_2NO_3$ , crystallises from glacial acetic acid in stunted orthorhombic prisms, and melts and decomposes at 159°.

In discussing his results, the author emphasises the fact that, whereas the preparation of derivatives of toluquinonemeto-xime gives rise to two stereoisomerides, the corresponding derivatives of the orthoxime exist only in one form; it is suggested, as a possible explanation, either that, in the latter case, the proximity of the side-chains prevents the formation of a space-isomeride, or that isomeric substances exist which cannot be distinguished by the ordinary methods. Since no trace of the orthoxime is formed on treating toluquinone with hydroxylamine hydrochloride, Kehrman's rule (Abstr., 1889, 243) concerning the influence of side-chains in quinones on the position taken by the entering isonitroso-group is confirmed; the latter's views of the space-isomerism of the quinoneoximes also explain the existence of stereoisomeric modifications in the cases dealt with above.

W. A. D.

**Beckmann's Transformation.** By KARL AUWERS and H. CZERNY (Ber., 1898, 31, 2692—2698).—The production of indazole derivatives by the action of glacial acetic acid with acetic anhydride and hydrogen chloride on the oximes of aromatic orthamidoketones (compare Auwers, Abstr., 1896, i, 503), suggested the possibility of obtaining analogous indoxazenes,  $C_6H_4 \begin{smallmatrix} \text{CR} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} N$ , from the oximes of aromatic orthohydroxyketones. Contrary to expectation, however, the oxime of unsymmetrical orthohydroxymetamethylbenzophenone,

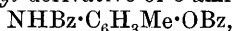


undergoes the Beckmann transformation, yielding benzenyl-3-amidoparacresol,  $C_6H_3Me \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ O \end{smallmatrix} CPh$ , and the anilide of 4-hydroxymetatoluic acid. In addition to Beckmann's mixture, zinc chloride, phosphorus pentachloride, phosphoric anhydride, and anhydrous copper sulphate induce this change, which also occurs when the substance is distilled under ordinary and reduced pressures; the action of copper sulphate gains in interest from the fact that it has, hitherto, been

employed when transformation of an oxime is to be avoided. The result of heating the oxime of orthohydroxymetamethylbenzophenone gives support to Beckmann's opinion that the transformation of oximes into amides is an instance of catalytic action (Abstr., 1894, i, 240).

The *oxime* of unsymmetrical orthohydroxymetamethylbenzophenone,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CPh}\cdot\text{NOH}$ , crystallises from glacial acetic acid in small, white needles, and melts at  $126\text{--}128.5^\circ$ .

*Benzenyl-3-amidoparacresol*,  $\text{C}_6\text{H}_3\text{Me}\langle\text{N}\rangle\text{CPh}$ , obtained by the action of Beckmann's mixture, melts at  $104^\circ$ ; concentrated hydrochloric acid at  $150\text{--}160^\circ$  converts it into benzoic acid and 3-amidoparacresol. The *dibenzoyl* derivative of 3-amidoparacresol,



crystallises from alcohol in white leaflets and melts at  $190\text{--}191^\circ$ ; hydrochloric acid precipitates from the solution in caustic soda the *benzoyl* derivative,  $\text{NHBz}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OH}$ , which crystallises in nacreous leaflets and melts at  $191^\circ$ . When either of these compounds is boiled during a few minutes, it yields benzenyl-3-amidoparacresol.

The anilide of 4-hydroxymetatoluic acid, obtained by the action of zinc chloride on the oxime of orthohydroxymetamethylbenzophenone, melts at  $158\text{--}159^\circ$ , and not at  $53^\circ$ , as stated by Bargioni; the *hydrogen phosphate* melts at  $187\text{--}189^\circ$ .  
M. O. F.

**Action of Alkyls of  $\beta$ -Ketonic Acids on Paraphenetidine.** By ERNESTO FOGLINO (*Chem. Centr.*, 1898, i, 501; from *Ann. Chim. Farm.*, 26, 535—541).—By the action of paraphenetidine on ethylic benzoylacetate at  $120\text{--}130^\circ$ , alcohol and benzoylacetophenetidine,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Bz}$ , are formed; the latter crystallises from alcohol in white needles, melts at  $139\text{--}140^\circ$ , and is insoluble in cold water. With the ethylic salts of acetoacetic, methylacetoacetic, diethylacetoacetic, benzoylacetoacetic, and acetylsuccinic acids, paraphenetidine at  $140\text{--}150^\circ$  yields alcohol, a ketone, and Wenghöfer's paradiphenetolcarbamide,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ . The last compound is also formed by the action of benzoylacetoacetamide on paraphenetidine.  
E. W. W.

**Action of Piperidine on Carbonates Derived from Phenols: Formation of Aromatic Urethanes.** By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1897, 125, 1107—1109).—When piperidine acts on carbonates derived from phenols, urethanes alone are produced, there is no formation of carbamide derivatives.

Piperidine and phenylic carbonate, when simply mixed together, form a *urethane*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{COOPh}$ , which melts at  $80^\circ$ , and dissolves in the ordinary organic solvents; it is hydrolysed by caustic potash into phenol and piperidine.

The *urethane*,  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{COO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , from guaiacol carbonate and piperidine, crystallises from alcohol in white prisms, melts at  $44^\circ$ , and boils at about  $330^\circ$ .

The corresponding  *$\beta$ -naphthyllic urethane*, produced by mixing together  *$\beta$ -naphthyllic carbonate* and piperidine, crystallises in needles and melts

at 107°. The  $\alpha$ -naphthyl compound has not yet been obtained crystalline.

When treated with concentrated sulphuric acid, these urethanes yield piperidine sulphate and a sulphonic acid of the corresponding phenolic compound. G. T. M.

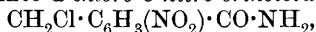
**Aromatic Urethanes of Conicine.** By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1898, 126, 481—483. Compare preceding abstract).—Conicine and phenyl carbonate, when heated together for 1 hour, form the *urethane*,  $C_8H_{16}N \cdot COOPh$ , a viscous liquid boiling at 325°; its rotation in alcoholic solution is  $[\alpha]_D + 3.66^\circ$ .

The *urethane*,  $C_8H_{16}N \cdot COO \cdot C_6H_4 \cdot OMe$ , is obtained in similar manner from guaiacol carbonate; it forms a viscous liquid boiling at 277°. The  $\alpha$ - and  $\beta$ -*naphthyl urethanes*,  $C_8H_{16}N \cdot COO \cdot C_{10}H_7$ , are very viscous liquids boiling above 300°.

All these substances are hydrolysed by caustic potash at 150°, and are decomposed by concentrated sulphuric acid with evolution of carbonic anhydride. G. T. M.

**Pseudophthalimidine and Orthocyanobenzylamine.** By SIEGMUND GABRIEL and WILLY LANDSBERGER (*Ber.*, 1898, 31, 2732—2740).—Kiel (*Inaug. Diss. Bonn.*, 1896) has shown that pseudophthalimidine probably has the constitution,  $NH \cdot C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown O \end{smallmatrix} CH_2$ , which was formerly assigned by Graebe to phthalimidine. The authors have examined the molecular weights of these compounds in order to ascertain whether they both correspond with this formula. Pseudophthalimidine itself is not adapted for this purpose, since it cannot be purified by distillation, and the corresponding nitro-derivative was, therefore, substituted for it.

Orthocyanobenzyl chloride is converted by nitration into 5-nitro-2-cyanobenzyl chloride,  $CH_2Cl \cdot C_6H_3(NO_2) \cdot CN$ , which forms yellowish crystals and melts at 94°. When heated with hydrochloric and acetic acids at 140—150°, it is converted into 5-nitrophthalide, a reaction which indicates the constitution of the compound. The nitro-compound can readily be converted by hydrolysis with sulphuric acid into  $\omega$ -chloro-5-nitro-orthotoluidine,



which crystallises in matted, snow-white needles melting at 228° when rapidly heated. When heated for some time at 110°, it is converted into 5-nitropseudophthalimidine,  $NO_2 \cdot C_6H_3 \begin{smallmatrix} \diagup CH_2 \\ \diagdown C(NH) \end{smallmatrix} O$ , which crystallises in needles melting at 158°. The *hydrochloride* decomposes in aqueous solution, forming ammonium chloride and nitrophthalide. The *picrate* melts at 158°, whilst the *platinochloride* crystallises in narrow, orange-yellow prisms and decomposes at about 120°, and the *aurichloride* crystallises well.

This compound and phthalimidine itself have the normal molecular weight, determined by the boiling point method. Hence it appears that phthalimidine has the constitution  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CH_2 \end{smallmatrix} NH$ , whilst

pseudophthalimidine receives the formula assigned to it by Kiel. When orthocyanobenzylphthalimide is heated with hydrochloric acid at 190—200°, a small amount of phthalimidine is formed. In former experiments, this was isolated as nitrosophthalimidine, the formation of which was, however, ascribed to the action of the nitrous acid on the orthocyanobenzylamine which is also present in the product. Renewed experiments have, however, shown that orthocyanobenzylamine is not attacked by nitrous acid, but that it is converted into phthalimidine by the continued action of acids. This formation of phthalimidine affords further evidence in favour of the formula ascribed to it above. Orthocyanobenzylamine is best obtained by heating orthocyanobenzylphthalimide with alcoholic potash. The *hydrochloride* decomposes at about 207°, whilst the *picrate* melts and decomposes at about 219°.

Alcoholic potash cannot be employed for the preparation of other amines from their phthalimide compounds; benzylphthalimide, for example, when treated in this way, does not yield the amine, but is converted into *benzylphthalaminic acid*,  $C_7H_7 \cdot NH \cdot CO \cdot C_6H_4 \cdot COOH$ , which crystallises in needles and melts and decomposes at 154°, benzylphthalimide being again produced. A. H.

**Diazomethane and Nitroso-acidamides.** By HANS VON PECHMANN (*Ber.*, 1898, 31, 2640—2646).—When nitrosomethylurethane is decomposed by alcoholic potash, only half the theoretical yield of diazomethane is obtained, and this is due to the fact that the remainder of the urethane is decomposed by the potash in the following ways. 1, Formation of nitrous acid and urethane,  $NO \cdot NMe \cdot COOEt + H_2O = HNO_2 + NHMe \cdot COOEt$ ; 2, formation of carbonic acid, nitrous acid, and methylamine,  $NO \cdot NMe \cdot COOEt + 2H_2O = OH \cdot COOEt + HNO_2 + NH_2Me$ . Nitrosoethylurethane, nitrosobenzylurethane, and nitrosobenzoylbenzylamine are decomposed in a similar manner, whilst it has been found that benzylamine acts as an alkali in the same way as the potash. *Nitrosoethylurethane*, prepared in the same way as the methyl derivative, is an oil which boils at 90° under a pressure of 42 mm. and has a sp. gr. = 1.0735 at 15°/15°. When treated with alcoholic potash, 20 per cent. of the theoretical amount of *diazoethane* is produced; this is very similar to diazomethane, but its solution in ether is of a darker colour. When nitrosoethylurethane is treated with benzylamine, nitrogen is evolved and benzylurethane produced, the diazoethane, which is, no doubt, the first product, being immediately decomposed. *Benzylurethane* crystallises in colourless plates melting at 44°, and is converted by nitrous acid into *nitrosobenzylurethane*, which is a reddish-yellow oil, and cannot be distilled; when this is treated with alcoholic potash, it yields stilbene and benzylic methylic ether. *Nitrosobenzobenzylamide* crystallises in pinkish prisms, melts at 46—47°, and gradually decomposes when kept, yielding nitrogen and benzylic benzoate. When heated with alcohol, it decomposes in all the ways already described in the case of nitrosomethylurethane: (1) into benzoic acid and phenyldiazomethane, which appears in the product partly as benzylic ethylic ether, and partly as benzylic benzoate; (2) into nitrous acid and



benzoylbenzylamine; and (3) into benzoic acid, nitrous acid, and benzylamine.

Attempts to bring about the direct elimination of nitrogen from diazomethane by heating it, and by the use of powdered copper, platinum black, &c., proved unsuccessful. A. H.

**New Representatives of Primary Disazo-dyes of the Benzene Series.** By CARL BÜLOW and HANS WOLFS (*Ber.*, 1898, 31, 2775—2783, Compare Abstr., 1898, i, 308).—The following additional colouring matters have been prepared; they have the general formula  $\text{NMe}_2 \cdot \text{C}_6\text{H}_2(\text{OH})(\text{N}_2\text{R}) \cdot \text{N}_2\text{R}'$  [ $\text{NMe}_2 : \text{OH} : \text{N}_2\text{R} : \text{N}_2\text{R}' = 1:3:4:6$ ], and the groups tabulated under 4 and 6 are the groups R and R' respectively; the method of preparation is that already indicated.

4.	6.	Colour.	Melting point.
Ph	1-C <sub>10</sub> H <sub>7</sub>	Dark red	178°
1-C <sub>10</sub> H <sub>7</sub>		Violet-red	176
1-C <sub>10</sub> H <sub>7</sub>	Ph	Dark brown	180—181
Ph	2-C <sub>10</sub> H <sub>7</sub>	Claret-red	176
2-C <sub>10</sub> H <sub>7</sub>		Brown	196
2-C <sub>10</sub> H <sub>7</sub>	Ph	Brown	154
2-C <sub>10</sub> H <sub>7</sub>	1-C <sub>10</sub> H <sub>7</sub>	Black	185—186
2-C <sub>6</sub> H <sub>4</sub> Me	2-C <sub>6</sub> H <sub>4</sub> Me	Dark green	132
1-C <sub>10</sub> H <sub>7</sub>	2-C <sub>10</sub> H <sub>7</sub>	Dark brown	182
2-C <sub>6</sub> H <sub>4</sub> Me	2-C <sub>6</sub> H <sub>4</sub> Me	Dark green	187
2-C <sub>10</sub> H <sub>7</sub>	1-C <sub>10</sub> H <sub>7</sub>	Green	182
4-C <sub>6</sub> H <sub>4</sub> Me	4-C <sub>6</sub> H <sub>4</sub> Me	Dark brown	154—155
1-C <sub>10</sub> H <sub>7</sub>	2-C <sub>10</sub> H <sub>7</sub>	Red	153
4-C <sub>6</sub> H <sub>4</sub> Me	4-C <sub>6</sub> H <sub>4</sub> Me	Dark green	180
2-C <sub>10</sub> H <sub>7</sub>	1-C <sub>10</sub> H <sub>7</sub>	Dark red	147—148
2:4-C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub>	2:4-C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub>	Dark red	141
1-C <sub>10</sub> H <sub>7</sub>	2-C <sub>10</sub> H <sub>7</sub>	Red	175
2:4-C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub>	2:4-C <sub>6</sub> H <sub>3</sub> Me <sub>2</sub>	Dark green	171—172
2-C <sub>10</sub> H <sub>7</sub>			

C. F. B.

**Ketochlorides and Orthodiketones of Phenylazimido-benzene and Phenyl- $\psi$ -azimidobenzene.** By THEODOR ZINCKE and E. PETERMANN (*J. pr. Chem.*, 1898, [ii], 58, 234—244. Compare Abstr., 1898, i, 537).—The paper contains a preliminary account (without experimental details) of experiments with phenylazimido-benzene and phenyl- $\psi$ -azimidobenzene, carried out on similar lines to those already described with azimidobenzene (*loc. cit.*). Like the latter substance, they can be converted into ketochlorides and orthodiketones, possessing a strong analogy to those derived from azimido-benzene. The analogy is not complete, however, for the presence of the phenyl group, and the difference in constitution of the nitrogen ring, exert an influence on the results. For example, the phenyl group of the azimido-derivative does not react with chlorine, whereas substitution takes place in the phenyl group of the  $\psi$ -derivative.

A. W. C.

**Hydrazides of Meta- and Para-bromobenzoic Acid.** By THEODOR CURTIUS and EDUARD PORTNER (*J. pr. Chem.*, 1898, [ii], 58, 190—205. Compare preceding abstract).—*Metabromobenzhydrazide*,  $C_6H_4Br \cdot CO \cdot NH \cdot NH_2$ , prepared from hydrazine hydrate and ethylic metabromobenzoate according to directions already given (*J. pr. Chem.*, [ii], 50, 295), forms long, glistening, silken needles, melts at  $151^\circ$ , is soluble in alcohol, but almost insoluble in ether, chloroform, and benzene, and reduces Fehling's solution and ammoniacal silver nitrate in the cold. The *hydrochloride* forms small leaflets melting and giving off gas at  $248^\circ$ ; the *sodium salt*, small plates; and the *acetyl derivative* colourless, silken prisms melting at  $169^\circ$ .

*Benzylidenemetabromobenzhydrazine*,  $CHPh \cdot N \cdot NH \cdot CO \cdot C_6H_4Br$ , prepared by the action of benzaldehyde on the hydrazide, crystallises from alcohol in beautiful, long, colourless needles melting at  $105^\circ$ ; boiling dilute mineral acids decompose it into its components. The corresponding *orthohydroxybenzylidene* compound forms tufts of colourless needles melting at  $192^\circ$ , and the *acetone* [ $\beta$ -propylidene] derivative, small needles melting at  $88.5^\circ$ . *Dimetabromobenzhydrazide*,  $(NH \cdot CO \cdot C_6H_4Br)_2$ , obtained by the action of iodine on the bromobenzhydrazide, crystallises from glacial acetic acid in small, glistening needles melting at  $265^\circ$ . When boiled with dilute mineral acids, it is converted into bromobenzoic acid and a hydrazine salt.

*Metabromobenzazide*,  $C_6H_4Br \cdot CO \cdot N_3$ , obtained by the action of nitrous acid on bromobenzhydrazide, is a colourless oil with an unbearable odour producing tears, and explodes violently when heated in a test tube.

*Metadibromodiphenylcarbamide*,  $CO(NH \cdot C_6H_4Br)_2$ , prepared from the azide by boiling with water, forms long, colourless, silken prisms melting at  $262^\circ$ . It is volatile without decomposition, sublimes in small needles, and, when boiled with acids, is decomposed into metabromaniline and carbonic anhydride.

*Ethylic metabromophenylcarbamate*,  $C_6H_4Br \cdot NH \cdot COOEt$ , obtained by the action of absolute alcohol on metabromobenzazide, is a thick, colourless oil boiling at  $193$ — $194^\circ$  under a pressure of 17 mm., and is decomposed into its components by concentrated acids. The corresponding *methylic salt* is a colourless oil boiling at  $165$ — $167^\circ$  under a pressure of 75 mm.

The following corresponding *para*-compounds are also described.

*Bromobenzhydrazide*, long, colourless prisms melting at  $164^\circ$ ; its *hydrochloride*, small, glistening needles melting at  $262^\circ$ ; *acetone*-[ $\beta$ -propylidene]*bromobenzhydrazide*, long needles melting at  $194.5^\circ$ ; *benzylidenebromobenzhydrazide*, colourless, silken prisms melting at  $235^\circ$ ; *bromobenzazide*, colourless plates melting at  $46^\circ$ ; *ethylic bromophenylcarbamate*, long, white needles melting at  $81^\circ$ ; the corresponding *methylic salt* melts at  $81^\circ$ ; *dibromodiphenylcarbamide*, clusters of nacreous needles melting at  $274^\circ$ ; and *bromophenylbromobenzoylsemicarbazide*,  $C_6H_4Br \cdot NH \cdot CO \cdot N_2H_2 \cdot C_6H_4Br$ , microscopic plates melting at  $248^\circ$ .

When parabromobenzazide is dissolved in carbon tetrachloride, and bromine added, a colourless, crystalline substance, probably dibromocarbamil, is obtained.

A. W. C.

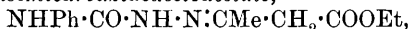
**Phenylsemicarbazide.** By THEODOR CURTIUS and ADOLF BURKHARDT (*J. pr. Chem.*, 1898, [ii], 58, 205—233. Compare Abstr., 1896, i, 647).—In continuance of the researches of Curtius and Hofmann (*loc. cit.*), it is now shown that phenylcarbamazide does not undergo rearrangement, as do ordinary acid azides of the type  $RCON_3$ . When heated with water in sealed tubes, it is completely converted into carbonic anhydride, diphenylcarbamide and hydrazoic acid; alcohol decomposes it into hydrazoic acid and phenylurethane; aniline produces the carbanilide, and bromine gives *parabromophenylcarbamazide*,  $C_6H_4Br \cdot NH \cdot CO \cdot N_3$ , separating from alcohol in rhombic crystals melting at  $126^\circ$ , which are acted on by water, with production of paradibromocarbanilide.

The solid, microcrystalline product formed on adding sodium nitrite to an aqueous solution of oxalhydrazide hydrochloride is not a product of the rearrangement of the oxazide, but the dihydrazide of oxalic acid, produced by the oxidation of the hydrazide.

Phenylsemicarbazide may be obtained by the action of hydrazine hydrate on (a) the phenylurethanes,  $NHPh \cdot COOR + N_2H_5OH = NHPh \cdot CO \cdot NH \cdot NH_2 + ROH + H_2O$ ; (b) on mono- or di-phenylcarbamide,  $CO(NHPh)_2 + N_2H_5 \cdot OH = NHPh \cdot CO \cdot NH \cdot NH_2 + NH_2Ph + H_2O$ ; (c) on phenylcarbimide. The best yields are obtained from diphenylcarbamide, all the other reactions being more or less complicated, and the isolation of the base difficult.

Phenylsemicarbazide *hydrochloride* forms colourless, transparent prisms melting at  $215^\circ$ ; the *sodium* compound crystallises in yellowish needles, and the *acetyl* derivative in colourless needles melting at  $169^\circ$ .

*Ethyl phenylsemicarbazideacetoacetate*,



formed by the interaction of ethylic acetoacetate and the semicarbazide, crystallises from alcohol in small, colourless needles melting at  $151^\circ$ .

*Hydrazidicarbonanilide*,  $NHPh \cdot CO \cdot NH \cdot NH \cdot CO \cdot NHPh$ , obtained by the action of iodine or of heat alone on phenylsemicarbazide, crystallises from glacial acetic acid in long, colourless prisms melting at  $245^\circ$ , without decomposition, is with difficulty soluble in the ordinary organic solvents, and possesses basic properties. When heated with hydrochloric acid in sealed tubes, at  $180$ — $200^\circ$ , it is completely converted into carbonic anhydride, aniline, and hydrazine hydrochloride. Bromine acts on it in glacial acetic acid solution, forming a *tetrabromo*-compound,  $C_{14}H_{12}N_4Br_4$ , crystallising in needles and melting at  $215$ — $218^\circ$ .

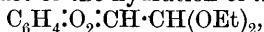
*Azo-dicarbonanilide*,  $N_2(CO \cdot NHPh)_2$ , produced by the action of nitric acid on hydrazidicarbonanilide, crystallises from acetone in bunches of dark red needles melting at  $182$ — $183^\circ$ . On rubbing, the substance becomes strongly electric, and is reconverted into hydrazidicarbonanilide by boiling with acids, alkalis, or tin and hydrochloric acid.

*Phenylcarbamazinide*,  $NHPh \cdot CO \cdot N$ ., prepared by the action of

sodium nitrite on an aqueous solution of phenylsemicarbazide hydrochloride, crystallises in colourless leaflets melting at  $103-104^{\circ}$ .

A. W. C.

**Catecholglyoxal.** By CHARLES MOUREU (*Compt. rend.*, 1898, 127, 324—326).—The compound,  $C_8H_8O_4$ , obtained by J. Hesse by boiling with dilute sulphuric acid the product,  $C_6H_4 \cdot O_2 \cdot CH \cdot CH(OEt)_2$ , prepared by the action of dichloroacetal on disodiumcatechol, is identical with the hydroxyphenoxyacetic acid obtained by the author under similar conditions from dicatecholacetylenic ether. It is clear that, although the aldehyde catecholglyoxal has not been isolated, it must be the first product of the hydration of the compound



and hence may be assumed to be an intermediate product in the hydration of catechol acetylenic ether, since the final product is the same in both cases (compare this vol., i, 125).

C. H. B.

**Benzoyl Derivatives of Acetonitrile and Paratoluoylacetonitrile.** By O. SEIDEL (*J. pr. Chem.*, 1898, [ii], 58, 129—159).—Benzoylacetonitrile (cyanacetophenone) is best obtained by the action of concentrated hydrochloric acid on benzacetodinitrile. Obregia (Abstr., 1892, ii, 324) obtained from it, by the action of phenylhydrazine, a yellow, crystalline substance melting at  $134-135^{\circ}$ , whereas Burns (Abstr., 1893, i, 314), by the action of phenylhydrazine on benzacetodinitrile, obtained yellow needles melting at  $121^{\circ}$ , although the reaction should give the same substance as that obtained by Obregia. The author now shows that the two substances are identical, and must be regarded as the *phenylhydrazone* of cyanacetophenone melting at  $146-147^{\circ}$ , the difference in the observed melting points being accounted for by the fact that, on warming, or on exposure to air, or by repeated crystallisation from dilute alcohol or chloroform, it is partially converted into an isomeride, 1:3-diphenyl-5-imidopyrazoline,  $C_{15}H_{13}N_3$ , crystallising in white, rhombic plates and melting at  $129.5^{\circ}$ ; this cannot be reconverted into the phenylhydrazone, than which it is much more stable, and possesses basic properties.

The *hydrochloride* is not stable in air, and the *platinochloride* crystallises in large, prismatic needles melting and decomposing at  $191^{\circ}$ . Both isomerides, when treated with acetic anhydride, give the same *monacetyl* derivative, crystallising from benzene in beautiful, white needles melting at  $149^{\circ}$ .

When the phenylhydrazone is treated with nitrous acid in ether, benzene, alcohol, or chloroform solution, nothing but tarry products are produced, but when dissolved in acetic acid, whereby it is converted into its isomeride, two substances are formed which can be separated by the difference in their solubilities in acetic acid or benzene; the one is the true *nitroso*-derivative of diphenylimidopyrazoline,  $C_{15}H_{12}N_4O$ , crystallising from benzene in dark red, glistening prisms melting at  $207^{\circ}$ , which, when heated with concentrated hydrochloric acid, is converted into 4-isonitroso-1:3-diphenylpyrazolone (compare Knorr and Klotz,

(Abstr., 1887, 1121), and the other, of the composition  $C_{30}H_{23}N_7$ , crystallises from glacial acetic acid in canary-yellow needles, melting at  $217^\circ$ . It is not acted on by concentrated sulphuric acid or hydrochloric acid when heated with it in sealed tubes at  $160^\circ$ , and is probably formed by the condensation of 1 molecule of the red substance with 1 molecule of the imidopyrazoline.

Phenylhydrazine reacts with paratoluacetodinitrile, forming a *phenylhydrazone* crystallising in yellow needles and melting at  $153^\circ$ . When heated, or dissolved in acetic acid, it is converted into the isomeric 1-phenyl-3-paratolyl-5-imidopyrazoline, from which, by the action of nitrous acid a *red* substance,  $C_{16}H_{14}N_4O$ , melting at  $232^\circ$ , and a *yellow* substance,  $C_{32}H_{27}N_7$ , melting at  $212^\circ$ , are produced.

Burns (*loc. cit.*) and Obregia (*loc. cit.*) have stated that cyanacetophenoneoxime is only stable in the form of its isomeride phenylisoxazoloneimide, whereas Probst believes the oxime of paratolylacetodinitrile to be a true oxime. The author cannot substantiate Probst's conclusions, and regards the substance as  $\gamma$ -paratolylimidoisoxazoline.

*Cyanacetophenone diphenylhydrazone*,  $C_{21}H_{17}N_3$ , obtained by the action of diphenylhydrazine on an alcoholic solution of cyanacetophenone, crystallises from dilute alcohol in yellow prisms melting at  $148^\circ$ ; it cannot be converted into an isomeride either by the action of heat or by dissolving it in glacial acetic acid.

*3-Phenyl-5-imidopyrazoline*,  $C_9H_9N_3$ , produced by the action of hydrazine sulphate on cyanacetophenone, forms white crystals melting at  $125^\circ$ . The *hydrochloride* crystallises in small needles, and the *platinochloride* forms large, yellow prisms melting and decomposing at  $225^\circ$ .

*1:3:5-Triphenyl-4-cyanopyrazole*,  $C_{22}H_{15}N_3$ , obtained by the interaction of dibenzoylacetonitrile and phenylhydrazine hydrochloride, crystallises from alcohol in white needles melting at  $189^\circ$ , is insoluble in potassium hydroxide, is not attacked by hydrochloric acid when heated with it in sealed tubes at  $160^\circ$ , or by sulphuric acid, in which it is soluble, and does not form a *platinochloride*; when hydrolysed, it is converted into *1:3:5-triphenyl-4-pyrazolecarboxylic acid*, which crystallises in white needles melting at  $238^\circ$ , and when heated alone, is changed into *1:3:5-pyrazole*, with loss of carbonic anhydride.

When the silver salt of dibenzoylacetonitrile is treated with methylic iodide, the *methylic* salt is obtained in small, yellow needles melting at  $117$ – $118^\circ$ ; it is neutral, and is readily decomposed by water into dibenzoylacetonitrile and methylic alcohol.

*Tribenzoylacetonitrile*,  $CN \cdot CBz_3$ , or  $CN \cdot CBz : CPh \cdot OBz$ , obtained from the above silver salt by the action of benzoic chloride, forms compact, white crystals melting at  $138^\circ$ . Alkalis decompose it at once into dibenzoylacetonitrile and benzoic acid; aniline gives the corresponding *anilide* crystallising from alcohol in silken needles melting at  $165^\circ$ , and phenylhydrazine produces *1:3:5-triphenyl-4-cyanopyrazole*.

During the original reaction (benzoic chloride and acetonitrile), a *substance*,  $C_{17}H_{12}N_2O$ , is also produced, crystallising in golden needles melting at  $204^\circ$ ; it could not be obtained in quantity sufficient for complete investigation.

A. W. C.

**Condensations with Phenylacetone [Benzyl Methyl Ketone].**

II. By GUIDO GOLDSCHMIEDT and GUSTAV KNÖPFER (*Monatsh.*, 1898, 19, 406—426. Compare Abstr., 1898, i, 31).—The ketone,  $C_{16}H_{15}ClO$ , obtained by the action of hydrochloric acid on a mixture of benzyl methyl ketone and benzaldehyde, may be made to yield stilbene by distillation with lime. It dissolves gradually in cold, strong sulphuric acid, giving a colourless solution, which becomes yellow and finally brown when warmed.

When heated with an alcoholic solution of hydroxylamine hydrochloride, chlorobenzylphenylacetone, as the author terms the above ketone, yields an *oxime*,  $C_{16}H_{15}NO$ , which crystallises in beautiful, colourless, silky needles, melts at  $153^{\circ}$ , and is insoluble in alkalis or acids; when boiled with acetic anhydride, it affords a *substance*, possibly an acetyl derivative, which crystallises from alcohol in beautiful, white needles, and melts at  $92^{\circ}$ .

When chlorobenzylphenylacetone is warmed, in alcoholic solution, with an equal weight of potassium cyanide, a *compound*,  $C_{17}H_{15}NO$ , is produced which crystallises from alcohol in needles and melts at  $193^{\circ}$ ; it sublimes without decomposing, and dissolves in strong sulphuric acid, giving a yellow solution which, when warmed, exhibits a feeble violet fluorescence. It was not possible to obtain the corresponding acid by hydrolysis.

The ketone,  $C_{16}H_{14}O$  (m. p. =  $53^{\circ}$ , *loc. cit.*), yields a thick oil on distillation with lime, but stilbene could not be detected in it. The ketone dissolves in sulphuric acid, giving an emerald green solution, which assumes a bluish-violet fluorescence when warmed. It is at once destroyed by permanganate solution, but is not appreciably affected by potassium hydroxide, or dilute alcoholic hydrochloric acid. It does not yield a crystallisable additive product with bromine.

The ketone,  $C_{16}H_{14}O$  (m. p. =  $71^{\circ}$ ), comports itself towards permanganate and on distillation exactly like its isomeride. Its solution in sulphuric acid is lemon-yellow, and, when warmed, becomes red, exhibiting a strong green fluorescence. It evolves the odour of benzaldehyde when warmed with alcoholic hydrochloric acid, and the solution on cooling, especially after dilution, deposits oily drops and crystals of the unaltered substance. The *dibromide*,  $C_{16}H_{14}OBr_2$ , made by adding bromine to a solution of the ketone in chloroform, crystallises in beautiful, silky needles, melts at  $93^{\circ}$ , and dissolves very readily in ether and benzene, but only sparingly in alcohol and light petroleum.

Triphenyltetrahydro- $\gamma$ -pyrone, when warmed with alcoholic hydrochloric acid, is decomposed into benzaldehyde and the ketone melting at  $71^{\circ}$ ; the inverse change is effected by shaking a mixture of benzaldehyde and the unsaturated ketone with aqueous potash during 48 hours; the saturated ketone does not afford the pyrone derivative under these conditions; under certain circumstances, the substance melting at  $175^{\circ}$  is also formed by this process of condensation (*loc. cit.*). The analysis and molecular weight of the latter compound points to the formula  $C_{41}H_{38}O_3$ , hence its formation from benzyl methyl ketone and benzaldehyde is probably effected in similar manner to that of dibenzylidenetriacetophenone, by the condensation of acetophenone and benzaldehyde; its constitution is probably, therefore,

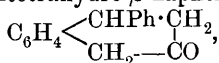
COMe·CPh(CHPh·CHPh·COMe)<sub>2</sub>. Benzylidenetriphenylacetone dissolves in strong sulphuric acid, and forms a lemon-yellow solution, which darkens spontaneously and becomes ruby-red when warmed.

When hydrogen chloride is passed into an imperfectly cooled mixture of benzyl methyl ketone and benzaldehyde, a substance, C<sub>25</sub>H<sub>22</sub>O, is sometimes obtained; this forms yellowish crystals, melts at 140°, and may be distilled without decomposing. It is probably produced by the condensation of an intermediate 1:5-diketone in the usual manner, being, therefore, 1-methyl-2:3:4-triphenylcyclo-Δ<sup>6</sup>-hexenone-5, CMe<CHPh·CHPh>CHPh. It gives an oxime, C<sub>25</sub>H<sub>21</sub>NO,

which forms aggregates of crystals, melts at 204°, and dissolves sparingly in alcohol, but readily in other media.

Dibenzyl ketone and benzaldehyde condense in presence of dry hydrogen chloride, forming a substance which has the composition C<sub>22</sub>H<sub>19</sub>ClO, and is, therefore, the hydrogen chloride additive product of benzylidene dibenzyl ketone; it melts at 143°, and, on distillation, yields phenylacetic chloride and stilbene.

Of the above isomeric ketones, C<sub>16</sub>H<sub>14</sub>O, that melting at 53° is saturated and produced by a ready elimination of hydrogen chloride from the substance C<sub>16</sub>H<sub>15</sub>ClO, and is, therefore, in all probability a cyclic compound, 1-phenyltetrahydro-β-naphthenone,



whilst the isomeric unsaturated ketone (m. p. = 71°) probably has the constitution CHPh:CPh·COMe.

The hydrocarbon melting at 120°, which was obtained from benzaldehyde and benzyl methyl ketone by the use of sulphuric acid (*loc. cit.*), turns out to be stilbene (compare Miller and Rohde, *Abstr.*, 1890, 978). A. L.

**Solubilities of the Nitrobenzoic Acids.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, 17, 247—258).—The following table gives the solubilities of ortho-, meta- and para-nitrobenzoic acids in water, chloroform, and absolute alcohol at temperatures of 15°, 25°, and 35°; the numbers represent grams of acid dissolved in 100 grams of the solvent, except in the case of alcohol, when they represent gram-molecules per litre.

Nitrobenzoic acid.	Water at			Chloroform at			Absolute alcohol at 15°.
	15°.	25°.	35°.	15°	25°.	35°.	
Ortho .....	0·625	0·744	1·141	1·06	1·13	1·59	2·25
Meta .....	0·238	0·305	0·477	3·45	4·70	6·31	2·83
Para .....	0·0213	0·0235	0·0419	0·088	0·114	0·156	0·118

The solubility in water of a mixture of the para-acid with either the ortho- or meta-acid is approximately equal to that calculated

from Nernst's theory of the diminution in solubility of one substance in presence of another having an ion in common with it. An increase of solubility of the three acids occurs, however, when they are all present simultaneously in solution; and the same is true of a mixture of the ortho- and meta-acids. To explain this anomaly, combination is assumed to take place between the substances present together (compare Le Blanc and Noyes, *Abstr.*, 1891, 388); this would elucidate the difficulty experienced in separating ortho- and meta-nitrobenzoic acids by crystallisation from water. W. A. D.

**Piperonal Derivatives.** By S. BAUDE and ALBERT REYCHLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 616—618).—*Ethylic methylenedioxy-cinnamate*,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}:\text{CH} \cdot \text{COOEt}$ , obtained by the action of metallic sodium on a mixture of piperonal and ethylic acetate, crystallises in needles melting at  $65-68^\circ$ , is soluble in alcohol and ether, and distils, with slight decomposition, at about  $317^\circ$ . Its *dibromide* forms colourless plates melting at  $84^\circ$ , and is readily soluble in ether or alcohol, but insoluble in light petroleum.

*Methylenedioxyphenylpropionic acid*,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{C}:\text{C} \cdot \text{COOH}$ , obtained when the dibromide is repeatedly boiled with alcoholic potash, crystallises from dilute alcohol in pale yellow needles, turns brown at  $145^\circ$ , and melts and decomposes at  $166^\circ$ .

*Methylenedioxyphenylacetylene*, obtained by heating the above acid with three to four times its weight of dry aniline at  $150-160^\circ$ , is a yellow oil. J. J. S.

**Condensation of Phthalaldehydic Acid with Acetone and Acetophenone.** By ARTHUR HAMBURGER (*Monatsh.*, 1898, 19, 427—455. Compare Goldschmidt, *Abstr.*, 1892, 179, and Hemmelmayr, *Abstr.*, 1893, i, 181, and 1894, i, 151).—Phthalaldehydic acid and acetone condense readily at  $40-60^\circ$  in presence of dilute soda; the liquid, after remaining for 24—48 hours, is acidified with hydrochloric acid, when the mixture acquires a milky appearance, and a gelatinous precipitate slowly forms. This is separated by filtration, washed, and dissolved in alcohol, from which, on cooling, *diphthalidedimethyl ketone*,  $(\text{CO} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH} \cdot \text{CH}_2)_2\text{CO}$ , crystallises in the form of white, felted needles which melt at  $156-157^\circ$ . On evaporating the filtrate from the above precipitate, or extracting it with ether, it yields a much larger quantity of a second substance, *phthalidedimethyl ketone*,  $\text{CO} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{COMe}$ , which crystallises from water in quadratic plates of considerable size and melts at  $67-68^\circ$ , dissolves readily in water, alcohol, ethylic acetate, and benzene, and more sparingly in chloroform and light petroleum. Both compounds dissolve slowly in cold, but readily in hot, potash, giving intensely yellow colorations; with bromine, they give substitution, not additive, compounds.

*Diphthalidedimethyl ketoxime*,  $\text{C}_{19}\text{H}_{15}\text{O}_5\text{N}$ , is nearly insoluble in water,



acetic acid, ethylic acetate, and benzene, and only very sparingly in alcohol, methylic alcohol, ether, acetone, and chloroform, but dissolves readily in cold potash, and is reprecipitated by acids; it is indistinctly crystalline, sinters at  $181^{\circ}$ , and melts at  $197-203^{\circ}$ .

When hydroxylamine acts on phthalidedimethyl ketone, two isomeric oximes,  $C_{11}H_{11}NO_3$ , are formed; one of these, obtained by acidifying the product with hydrochloric acid, crystallises from dilute alcohol in yellowish forms and melts at  $127-128^{\circ}$ ; it dissolves very readily in methylic or ethylic alcohol or ether, less readily in water, sparingly in benzene and chloroform, and is more easily soluble in alkali than in water. The second oxime is formed by dissolving the first in boiling water, from which it separates in white, felted leaflets, or by heating it for some at  $100^{\circ}$ ; it melts at  $59-61^{\circ}$ , and dissolves readily in the usual media and in alkalis. Both oximes, when treated with the "Beckmann mixture," give an oil and an acetyl compound,  $C_{13}H_{13}NO_4$ ; this forms slender needles, and on warming with fuming hydrochloric acid gives phthalidedimethyl ketone.

Phthalidedimethyl ketone reacts with phenylhydrazine and with bromine, hydrogen bromide being evolved in the latter instance; in neither case, however, is a crystalline compound produced.

Phthalaldehydic acid and acetophenone interact in presence of soda at  $40^{\circ}$ ; the product, *phenyl phthalidemethyl ketone*,  $\begin{matrix} C_6H_4 \\ COO \end{matrix} > CH \cdot CH_2 \cdot C(=O)Ph$ , crystallises from alcohol in long, white, felted needles, and melts at  $141-142^{\circ}$ . It dissolves instantly in warm alkalis, with a yellow coloration, and is sparingly soluble in water and ether, but dissolves somewhat readily in alcohol.

*Phenyl phthalidemethyl ketoxime*,  $C_{16}H_{13}NO_3$ , forms white needles, sinters at  $177^{\circ}$ , and melts at  $181-182^{\circ}$ ; a second substance is obtained simultaneously which is insoluble in soda, and decomposes, evolving gas, at  $180^{\circ}$  and melts at  $215^{\circ}$ . The former is somewhat readily soluble in alcohol, ether, and hot benzene, and is very unstable in presence of light, becoming yellow; potash quickly dissolves it, but it is deposited unaltered on adding an acid. When subjected to treatment with "Beckmann's mixture," it yields

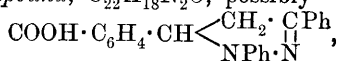
*3-carboxyphenyl-5-phenylisoxazoline*,  $CPh \begin{matrix} N \cdot O \\ \backslash \quad / \\ CH_2 \end{matrix} > CH \cdot C_6H_4 \cdot COOH$ .

Bromine acts on phenyl phthalidemethyl ketone, hydrogen bromide being evolved, but the product is not crystalline; it is not affected when shaken with benzylic chloride and aqueous soda.

When a mixture of phenylhydrazine and phenyl phthalidemethyl ketone is warmed on the water-bath, a substance of the composition  $C_{22}H_{18}N_2O_2$ , probably  $CO \begin{matrix} C_6H_4 \\ \backslash \quad / \\ N_2HPh \end{matrix} > CH \cdot CH_2 \cdot C(=O)Ph$ , is formed. This crystallises from alcohol in yellowish, glistening needles and melts at  $118-123^{\circ}$ ; it is very readily soluble in chloroform and alcohol, somewhat less readily in benzene and acetic acid, sparingly in ether, and is nearly insoluble in water. When heated with strong sulphuric acid, it becomes dark-red, but quickly dissolves, forming a yellow solution which soon becomes green, especially on the addition of a drop of

solution of ferric chloride. It does not reduce Fehling's solution, and is not affected by hot alkalis or by concentrated hydrochloric acid.

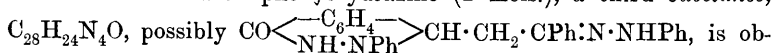
An isomeric compound,  $C_{22}H_{18}N_2O$ , possibly



is produced when phenyl phthalidemethyl ketone and phenylhydrazine are heated together in sealed tubes at  $170-190^\circ$  for 5 hours. It crystallises from alcohol in rosettes of needles and melts between  $170^\circ$  and  $200^\circ$ , is sparingly soluble in benzene, but dissolves readily in alcohol, ether, glacial acetic acid, and nitrobenzene. Its solution in concentrated sulphuric acid is red, becoming dark blue on the addition of a drop of ferric chloride, owing to the formation of a sparingly soluble blue compound, and on adding potassium dichromate, a violet coloration is produced which changes successively to dark blue, red, and yellowish-brown; in the latter instance, subsequent dilution of the liquid causes the separation of a red precipitate; dilute nitric acid instantly turns the substance blue; it does not reduce Fehling's solution. It dissolves in sodium carbonate solution, producing a liquid which readily forms a lather, and when excess of soda is used, a sodium salt is formed, which crystallises in beautiful, transparent needles.

The first isomeride, when heated in a closed tube at  $170^\circ$ , suffers almost complete conversion into the second.

When phenyl phthalidemethyl ketone is heated at  $170-190^\circ$  in sealed tubes with phenylhydrazine (2 mols.), a third substance,



which is nearly insoluble in water, alcohol, ether, and light petroleum, but dissolves readily in hot amyl alcohol, ethyl acetate, and glacial acetic acid, sinters at  $157^\circ$ , and melts at  $163-175^\circ$ . Sulphuric acid dissolves it, forming a dark green solution in which a trace of ferric chloride, potassium dichromate, or sodium nitrite produces a red coloration. It is insoluble in boiling alkalis, and does not reduce Fehling's solution.

A. L.

**Behaviour of Phthalide on Distillation with Lime.** By HANS KRCZMAR (*Monatsh.*, 1898, 19, 456—460).—A mixture of phthalide and lime was cautiously heated at about  $290^\circ$  in a long glass tube, through which a slow stream of hydrogen was passed; the distillate contained a clear liquid and a crystalline solid. The liquid portion consisted for the most part of benzene and probably, in part, of toluene, as on oxidation with chromic acid the odour of benzoic acid made itself perceptible. The solid substance was anthracene, probably contaminated with diphenyl.

A. L.

**Condensation of Malonic Acid with Aromatic Aldehydes by means of Ammonia and Amines.** By EMIL KNOEVENAGEL [and in part FR. BAEBENROTH and O. WOLLWEBER] (*Ber.*, 1898, 31, 2596—2619).—When malonic acid is warmed with substituted benzylidenebisalkylamines or benzylidenebisdialkylamines, interaction as a rule takes place readily, and acids of the acrylic or malonic series are produced. In the case of benzylidenebispiperidine and malonic acid, the action is represented by the equation  $CHPh(C_5NH_{10})_2 + CH_2(COOH)_2 = CHPh \cdot CH \cdot COOH + CO_2 + 2C_5H_{11}N$ .

Many benzylidenealkylamines act in a similar manner, but by using benzylidene- $\alpha$ (or  $\beta$ )-naphthylamine and benzylidenemetanitraniline, no cinnamic acid was obtained.

Hydrobenzamide reacts with malonic acid in a fashion which is analogous to the behaviour of other substituted benzylideneamines; the equation is  $N_2(CHPh)_3 + 3CH_2(COOH)_2 = 3CO_2 + 2NH_3 + 3CHPh:CH \cdot COOH$ .

Salicylideneaniline and malonic acid yield coumarincarboxylic acid, aniline, and water. It is not necessary to isolate the salicylideneaniline, mere addition of aniline to a solution of malonic acid and salicylic acid, or of the aldehyde to aniline malonate, being all that is required. Similar results with analogous trios of substances have shown that, in general, the order of interaction exerts only a quantitative influence on the product obtained.

The intermediate product in these reactions, namely, the alkylidene-malonic acid, may be isolated if the temperature of the reaction be kept sufficiently low, the optimum point depending on the nature both of the base and of the aldehyde employed. With ammonia, the temperature at which carbonic anhydride is eliminated is lower than where aniline is the condensing agent, and, in consequence, a smaller yield of alkylidenemalonic acid is obtained.

It is to be noted that the requisite proportion of base varies with the nature both of the base itself and of the aldehyde used; it is found, moreover, that, with some bases, little or none of the desired products are obtainable. The necessary duration of the action is also found to vary; in some cases, a short time only is advisable, and in others the reverse holds true.

The paper concludes with a detailed description of the experiments on which the foregoing statements are based, and the following substances are described for the first time.

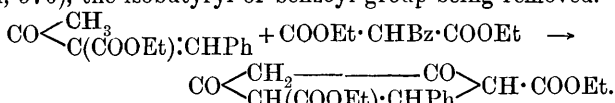
*Anisylidenemalonic acid* is obtained when anisaldehyde (1.3 grams) and normal ammonium malonate (1.4 grams) are covered with alcohol and the whole rapidly evaporated on the water-bath nearly to dryness, and is precipitated by means of sulphuric acid from its alkaline solution as a yellow, flocculent substance which melts and effervesces briskly at  $185-189^\circ$ ; it yields paramethoxycinnamic acid when boiled with alcohol.

*Piperonylidenemalonic acid* is made by warming piperonal with malonic acid and alcoholic ammonia (2 mols.) or with normal ammonium malonate. It is thrown down from its solution in soda, on acidification, as a white, flocculent precipitate, which melts and effervesces at  $190-195^\circ$ .

When a mixture of furfuraldehyde and malonic acid is cooled and treated with aniline, the whole soon solidifies and, on subsequently adding hydrochloric acid, crystals of a nitrogenous substance are deposited; this is sparingly soluble in water and dissolves in alcohol, forming a red solution which deposits violet crystals having a metallic lustre. It is completely destroyed by warm soda, and when warmed with sodium carbonate solution the colour is destroyed, but is restored on adding an acid.

A. L.

**Condensations of Acid Derivatives of Ethylic Malonate with Ethylic Benzylideneacetoacetate.** By EMIL KNOEVENAGEL and W. FABER (*Ber.*, 1898, 31, 2768—2772).—When ethylic benzylideneacetoacetate (Abstr., 1896, i, 232) and either ethylic isobutyrylmalonate (see below) or ethylic benzoylmalonate (Claisen, *Annalen*, 1896, 291, 72), are heated with a little alcohol until a homogeneous mixture has been formed, alcoholic potassium ethoxide then added, and the whole allowed to remain for several days, the product in both cases is diethylic 5-phenyl-1:3-diketocyclohexane-4:6-dicarboxylate (Abstr., 1894, i, 576), the isobutyryl or benzoyl group being removed.

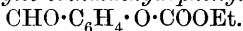


*Ethylic isobutyrylmalonate*,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}(\text{COOEt})_2$ , prepared from isobutyric chloride and ethylic sodiomalonate, boils at 133—134° under 14 mm., and at 126—127° under 10 mm. pressure. C. F. B.

**Condensing Action of Diethylamine.** By EMIL KNOEVENAGEL and W. FABER (*Ber.*, 1898, 31, 2773—2775).—When ethylic benzylideneacetoacetate,  $\text{CHPh} \cdot \text{CAc} \cdot \text{COOEt}$  (Abstr., 1896, i, 232), dissolved in a little alcohol, ethylic cuminyldeneacetoacetate (Abstr., 1898, i, 404), or benzylideneacetylacetone (Abstr., 1895, i, 50), is mixed with a little diethylamine and allowed to remain, the product is ethylic benzylidenediacetoacetate,  $\text{CHPh}(\text{CHAc} \cdot \text{COOEt})_2$  (Abstr., 1896, i, 210; Hantzsch, Abstr., 1886, 77), ethylic cuminyldenediacetoacetate or benzylidenediacetylacetone respectively. In the first case, a similar condensation took place, even when ethylic isobutyrylmalonate was present; no condensation with the latter substance occurred.

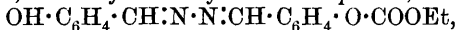
C. F. B.

**Orthaldehydophenoxy-acids.** By HERMANN CAJAR (*Ber*, 1898, 31, 2803—2811).—*Sodiosalicylaldehyde*,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{ONa}$ , was prepared by treating salicylaldehyde with sodium ethoxide in the presence of a large quantity of alcohol; it is lemon-yellow. When it is suspended in benzene and treated with ethylic chloroformate, and the product distilled under 90 mm. pressure, an oil comes over at 197°, which is presumably *ethylic orthaldehydophenylic carbonate*,

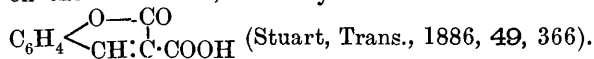


Alcoholic soda appears to hydrolyse this to the sodium salt, but the latter is at once decomposed by water, with formation of salicylaldehyde; the ethylic salt forms, however, a yellowish *phenylthylidrazone* melting at 101—102°, and with aqueous semicarbazide hydrochloride, a yellow *product* melting at 111°, which apparently has the composition  $\text{COOEt} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt}$ ; with aqueous hydrazine hydrate, it yields *salicylaldehyde hydrazone*,  $\text{NH}_2 \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , melting at 96° (this can also be obtained by adding a solution of hydrazine hydrate in dilute alcohol to an alcoholic solution of salicylaldehyde; when treated with acids, it yields Curtius and Jay's hydroxybenzalazine [Abstr., 1889, 393]); with salicylalde-

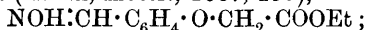
hyde hydrazone, the ethylic salt yields a *compound*,



which melts at  $114-115^\circ$ , and forms hydroxybenzalazine when treated with acids (salicylaldehyde hydrazone also forms a *compound*, melting at  $113-114^\circ$ , with ethylic acetoacetate); with hydrazine sulphate in aqueous solution, it forms the *compound*  $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt})_2$ , which is bright yellow and melts at  $109-110^\circ$ . With hydroxylamine, the ethylic salt does not react; by warming salicylaldoxime with ethylic chloroformate in concentrated alcoholic solution, a *compound* melting at  $69.5^\circ$  is obtained, but this, probably, has the constitution  $\text{COOEt} \cdot \text{O} \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , for salicylaldehyde itself does not react in an analogous fashion. With ethylic malonate, after 3 hours heating on the water-bath, the ethylic salt forms coumarincarboxylic acid,



Orthaldehydophenoxyacetic acid (Rössing, Abstr., 1885, 388) was prepared by heating salicylaldehyde (1 mol.) with monochloroacetic acid (1 mol.) and aqueous caustic soda (2 mols.) of sp. gr. = 1.2; when boiled with 3 per cent. methyl alcoholic hydrochloric acid, it yields the *methylic* salt,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOMe}$ , which melts at  $55-56^\circ$ , and forms a yellow *hydrazone*,  $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOMe})_2$ , melting at  $159-160^\circ$  (the allied opianic acid yields a *pseudo-salt*; compare Wegscheider, Abstr., 1892, 1208). With hydrazine hydrate, the acid gives a yellow *hydrazone*,  $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH})_2$ , which melts and decomposes at  $222^\circ$  (and not a phthalazone; compare Abstr., 1893, 371). When heated with hydroxylamine hydrochloride in 80 per cent. alcoholic solution, it yields the *ethylic* salt of orthaldoximephenoxyacetic acid (Elkan, Abstr., 1887, 259),



this melts at  $80^\circ$ .

C. F. B.

**An Isomeride of Diphenylene Bisulphide.** By P. GENVRESSE (*Bull. Soc. Chim.*, 1897, [iii], 17, 599—609. Compare Abstr., 1897, i, 240).—Phenylene bisulphide,  $(\text{C}_6\text{H}_4\text{S})_2$ , and an isomeric compound are obtained by the action of sulphur on benzene in the presence of aluminium chloride. The diphenylene bisulphide may be removed by treating with boiling glacial acetic acid until the residue gives an emerald green colour with concentrated sulphuric acid; the impure isomeride is then freed from excess of sulphur by washing with carbon bisulphide, and is dissolved in hot benzene, in which it is sparingly soluble and from which it separates on cooling in an amorphous condition. It melts at  $295^\circ$ , but begins to sublime even at lower temperatures, is sparingly soluble in hot benzene or chloroform, and is insoluble in most other solvents. Chromic acid oxidises it to *isodiphenylene disulphone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{SO}_2 \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{array} \text{C}_6\text{H}_4$ , which has not been obtained in a crystalline form, but is colourless, melts above  $360^\circ$ , is non-volatile, and only sparingly soluble in benzene, and when heated with concentrated sulphuric acid at  $200^\circ$  is converted into a substance soluble in water.

Fuming nitric acid oxidises the isobisulphide, yielding a mixture of products which have not been separated.

Fuming sulphuric acid yields a colouring matter *isotrioxypyhenylene bisulphide*,  $C_6S_2H_4O_3$ , when heated in sealed tubes at  $120-125^\circ$  with the isobisulphide; this compound is readily soluble in water or alcohol, giving red solutions, but is insoluble in benzene, chloroform, &c. In the solid state, it is brown, and with sulphuric acid gives a green solution; it may be obtained in a crystalline form from dilute sulphuric acid, but not from its aqueous or alcoholic solutions. Its aqueous solution, when mixed with a solution of sodium chloride, yields a brownish red precipitate, containing 70 per cent. of sodium chloride, and insoluble in alcohol. Sodium hydroxide turns the red, aqueous solution black, and a precipitate is slowly formed; a precipitate is also obtained with sodium carbonate, but no evolution of gas occurs. Barium hydroxide gives a dark brown precipitate, which, on adding an excess of hydroxide, becomes white; it is sparingly soluble in hot water, and its composition is represented by the formula  $C_6S_2H_2O_3Ba$ . The dark coloured precipitate can also be obtained in a crystalline form, and has the composition  $(C_6S_2H_3O_3)_2Ba$ .

A *triacetyl* derivative,  $C_6S_2O_3HAc_3$ , is obtained when the compound is boiled with acetic anhydride, but when the acetyl derivative is boiled with barium hydroxide, only one acetyl group is removed. The acetyl derivative forms a hard, black mass, soluble in water. The brown colouring matter gives azo-colours with aromatic amines.

J. J. S.

**Hydrazides and Azides of Sulphonic Acids.** By THEODOR CURTIUS and FERDINAND LORENZEN (*J. pr. Chem.*, 1898, [ii], 58, 160—189. Compare this vol., i, 136).—The ethereal salts of aromatic sulphonic acids,  $R'SO_3H$ , are completely hydrolysed on standing in the cold with hydrazine hydrate, the hydrazine first formed taking up water, with the production of the diammonium salt of the sulphonic acid, whereas the ethereal salts of sulphinic acids are not only hydrolysed, but decomposed by the reducing action of the diamide according to the following equation,  $4PhSO_2Et + 3N_2H_5 \cdot OH = 2Ph_2S_2 + 4EtOH + 7H_2O + 3N_2$ .

The hydrazides of the sulphonic acids can also be obtained by the action of hydrazine hydrate on the acid chloride; they reduce an ammoniacal solution of silver nitrate and Fehling's solution, and precipitate mercury from mercuric oxide. Iodine converts them into bisulphides and disulphoxides, but the latter could not be isolated, a similar reaction taking place when the sulphonehydrazides are heated. Like the hydrazides of the carboxylic acids, they are of a basic character, and condense with one molecule of an aldehyde or ketone. Acetic anhydride replaces one hydrogen of the hydrazine residue by an acetyl group, and nitrous acid converts them into the sulphonazides, which, unlike the azides of carboxylic acids, are not changed by heating with water or alcohol; neither are they acted on by bromine, and only with great difficulty by alkalis.

*Benzenesulphonehydrazide*,  $PhSO_2 \cdot NH \cdot NH_2$ , crystallises from alcohol in large plates or prisms melting and giving off gas at  $104-106^\circ$ .

The *hydrochloride* separates from alcohol in fine needles melting, with evolution of gas, at 150—152°, and the *sodium* salt,  $\text{PhSO}_2\cdot\text{NNa}\cdot\text{NH}_2$ , forms glistening plates.

*Benzyldenebenzenesulphonahydrazine*,  $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , formed by the action of benzaldehyde on the hydrazide, crystallises from dilute alcohol in colourless needles melting at 110—112°; the corresponding *acetone* [ $\beta$ -propylidene] derivative forms glistening leaflets melting at 143—145°, and the *acetyl* derivative crystallises in groups of glistening needles melting at 183—184°.

*Dibzenesulphonahydrazide*,  $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$ , produced by the interaction of benzenesulphonic chloride and benzenesulphonehydrazide, crystallises from alcohol or water in glistening needles melting and giving off gas at 228°. It reduces Fehling's solution and ammoniacal silver nitrate slowly in the cold, and is decomposed by iodine with evolution of nitrogen. Boiling dilute sulphuric acid decomposes it very slowly, but boiling alkalis decompose it readily with production of benzenesulphinic acid.

*Benzenesulphonazide*,  $\text{SO}_2\text{PhN}_3$ , is a yellowish oil which does not solidify when cooled, has a sweet odour, and when reduced with zinc dust and acetic acid is converted into benzenesulphonamide; it may be obtained by the action of nitric acid on benzenesulphonehydrazide.

*Diammonium benzenesulphonate*,  $\text{SO}_3\text{Ph}\cdot\text{N}_2\text{H}_5$ , obtained by the action of hydrazine hydrate on methylic benzenesulphonate, is a crystalline substance melting and decomposing at 175°. When further acted on by benzenesulphonic acid, it yields the *diammonium* salt,  $\text{N}_2\text{H}_4(\text{PhSO}_3\text{H})_2$ , crystallising from alcohol in glistening leaflets, which begin to decompose when heated to 250° and are not completely melted at 275°.

The corresponding *diammonium* salt of benzenesulphinic acid,  $\text{N}_2\text{H}_4(\text{Ph}_2\text{SO}_2\text{H})_2$ , crystallises from alcohol in glistening leaflets melting and decomposing at 139—141°.

$\beta$ -*Naphthylsulphonahydrazide* crystallises from alcohol in colourless needles melting and evolving gas at 137—139°, and when boiled with dilute sulphuric acid, is converted into  $\beta$ -naphthylsulphinic acid and hydrazine sulphate. The *hydrochloride* forms tufts of needles melting at 148—150°, and the *sodium* salt crystallises from alcohol with 1EtHO in glistening leaflets, which do not melt when heated to 275°.

*Benzyldene- $\beta$ -naphthylsulphonahydrazine*,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh}$ , obtained by the action of benzaldehyde on the sulphonahydrazide, crystallises in colourless needles melting and giving off gas at 150—152°, and the corresponding *acetone* [ $\beta$ -propylidene] derivative forms glistening plates melting and decomposing at 156—158°.

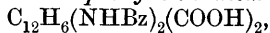
*Aceto- $\beta$ -naphthylsulphonahydrazide*,  $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{NHAc}$ , prepared by the action of acetic anhydride on the sulphonahydrazide, forms colourless, glistening needles melting at 208—209°.

*Di- $\beta$ -naphthylsulphonahydrazide*,  $(\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH})_2$ , formed by the interaction of the sulphonahydrazide with  $\beta$ -naphthylsulphonic chloride, crystallises from alcohol in slender needles melting and decomposing at 215°. Dilute sulphuric acid converts it into  $\beta$ -naphthylsulphonic acid and hydrazine sulphate. The *sodium* salt is a yellow powder, not melting when heated to 275°.

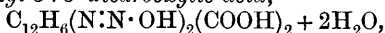
$\beta$ -Naphthylsulphonazide,  $C_{10}H_7SO_2 \cdot N_3$ , crystallises in white leaflets melting at 44—46°, but not exploding when heated to a higher temperature; when reduced with zinc dust and acetic acid, it is converted into  $\beta$ -naphthylsulphonamide.

Hydrazine hydrate acts on ethylic benzenesulphinate and methylic  $\beta$ -naphthylsulphinate, giving respectively phenylic bisulphide and  $\beta$ -naphthyllic bisulphide, and not the sulphinehydrazides. A. W. C.

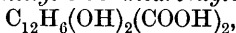
4 : 4'-Diamidodiphenyl-3 : 3'-dicarboxylic Acid. By CARL BÜLOW and ULRICH VON REDEN (*Ber.*, 1898, 31, 2574—2582).—This acid,  $C_{12}H_6(NH_2)_2(COOH)_2$ , is prepared by reducing orthonitrobenzoic acid in alkaline solution, and boiling the hydrazo-compound thus produced with concentrated hydrochloric acid. When it is dissolved in caustic soda, and the solution is shaken with benzoic chloride and kept cold meanwhile, 4 : 4'-dibenzamidodiphenyl-3 : 3'-dicarboxylic acid,



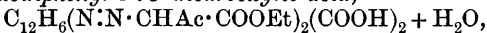
melting at 302—304°, is formed (the ammonium salt crystallises with  $2H_2O$ ) ; with acetic anhydride instead of benzoic chloride, the diacet-amido-compound is formed ; this melts at about 300°, and is converted into benzidine when it is boiled in glycerol solution. When the acid is dissolved in dilute hydrochloric acid and treated with sodium nitrite, and the hydrochloride formed is repeatedly dissolved in water and precipitated with a mixture of alcohol and ether, yellow 4 : 4'-tetrazodiphenyl-3 : 3'-dicarboxylic acid,



is obtained, and this, if boiled with 1 per cent. sulphuric acid, yields 4 : 4'-dihydroxydiphenyl-3 : 3'-dicarboxylic acid,



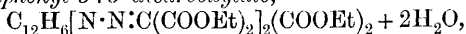
which melts at 302—305°, and yields 4 : 4'-dihydroxydiphenyl when heated with lime. When heated with bromine in hydrobromic acid solution, the tetrazo-acid yields a perbromide from which, by means of ammonia, greyish-green 4 : 4'-disdiazimidodiphenyl-3 : 3'-dicarboxylic acid,  $C_{12}H_6(N_3)_2(COOH)_2$ , decomposing at 165°, is obtained. Reduced by prolonged boiling with absolute alcohol, it yields diphenyl-3 : 3'-dicarboxylic acid, from which diphenyl can be obtained by heating with lime ; the latter acid forms a methylic and an ethylic salt, melting at 100—102° and 68° respectively, when it is dissolved in the corresponding alcohol and the solution is saturated with hydrogen chloride. When reduced with sodium sulphite solution, the tetrazo-acid yields diphenyl-4 : 4'-dihydrazine-3 : 3'-dicarboxylic acid,  $C_{12}H_6(NH \cdot NH_2)_2(COOH)_2$ , which is greyish to reddish-white, carbonises without melting when heated, and condenses with acetone at 40—50° to form the dark green disacetonediphenyl-4 : 4'-dihydrazone-3 : 3'-dicarboxylic acid,  $C_{12}H_6(NH \cdot N : CMe_2)_2(COOH)_2$ , melting at 265—267°. With phenol in strong caustic soda solution, the tetrazo-acid condenses to form the red 4 : 4'-disphenolazodiphenyl-3 : 3'-dicarboxylic acid,  $C_{12}H_6(N \cdot N \cdot C_6H_4 \cdot OH)_2(COOH)_2$  ; with ethylic acetoacetate in aqueous sodium acetate solution, it gives 4 : 4'-disethylic acetoacetate-azodiphenyl-3 : 3'-dicarboxylic acid,



melting at 275—278° ; with ethylic malonate in the presence of dilute alcohol and sodium acetate, it yields, after crystallisation of the



product from alcohol, brownish-yellow *ethylic 4 : 4'-disethylic mesoxalate-dihydratediphenyl-3 : 3'-dicarboxylate*,

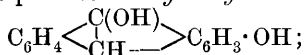


which melts at  $257^\circ$ .

C. F. B.

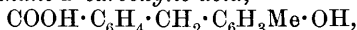
**Parahydroxyphenylphthalide, and its Conversion into Derivatives of Anthracene.** By AUGUSTIN BISTRZYCKI and D. W. YSSEL DE SCHEPPER (*Ber.*, 1898, 31, 2790—2802).—The hydroxyphenylphthalide,  $\text{CO} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , previously described (*Abstr.*, 1894, i, 600), yields *paramethoxyphenylphthalide* (Nourrisson, *Abstr.*, 1886, 1029) when methylated, and so must itself be a *para*-hydroxy-compound; similar conclusions may be drawn as to the constitution of the other substances described at the same time.

When parahydroxyphenylphthalide is reduced in alkaline solution by boiling with zinc dust, it yields *4-hydroxydiphenylmethane-2'-carboxylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , which melts at  $145\text{--}146^\circ$ ; its anhydrous *silver* salt was analysed. When it is dissolved in strong sulphuric acid at a temperature not exceeding  $30^\circ$ , and the solution is poured into water, the product is *2-hydroxyanthranol*,



this melts at  $221^\circ$ , and forms a *diacetyl* derivative melting at  $141\text{--}142^\circ$ ; the latter, when oxidised with chromic acid in acetic acid solution, yields a product identical with  $\beta$ -acetoxyanthraquinone.

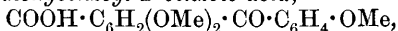
*Metacresylphthalide* yields a similar series of products. *4-Hydroxy-2-methyldiphenylmethane-2'-carboxylic acid*,



melts at  $168\text{--}169^\circ$ ; its anhydrous *barium* salt was analysed.

*2-Hydroxy-4-methylantranol*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{C}_6\text{H}_2\text{Me} \cdot \text{OH}$ , melts at  $224^\circ$ , its *diacetyl* derivative at  $172\text{--}173^\circ$ . *2-Acetoxy-4-methylantraquinone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_2\text{Me} \cdot \text{OAc}$ , melts at  $134\text{--}135^\circ$ , is yellow, and, when hydrolysed with alcoholic potash, yields the *2-hydroxy*-compound, which is yellow and melts at  $299\text{--}300^\circ$ , beginning to sublime at about  $200^\circ$ .

*4 : 5' : 6'-Trimethoxybenzoyl-2'-benzoic acid*,



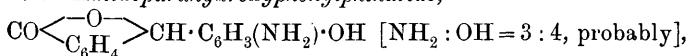
formed when hemipinic anhydride is heated in benzene solution with anisole and aluminium chloride and the product treated with hydrochloric acid, melts at  $215\text{--}216^\circ$ ; its anhydrous *silver* salt was analysed. When reduced with zinc dust in alkaline solution, it yields

*paramethoxyphenylpseudomeconine*,  $\text{CO} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2(\text{OMe})_2 \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ,

which melts at  $111\text{--}113^\circ$ . With zinc dust and hydrochloric acid in acetic acid solution, *4 : 5' : 6'-trimethoxydiphenylmethane-2'-carboxylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , melting at  $122\text{--}124^\circ$ , is obtained; strong sulphuric acid converts this into *2 : 3' : 4'-trimethoxydihydroanthrone*,  $\text{C}_6\text{H}_2(\text{OMe})_2 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_3 \cdot \text{OMe}$ , which melts at

169—170°, and is oxidised by chromic acid in acetic acid solution to 2:3':4'-trimethoxyanthraquinone,  $\text{C}_6\text{H}_2(\text{OMe})_2 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{OMe}$ , which is yellow, melts at 225°, and yields flavopurpurin when heated with aluminium chloride at 210°.

*Dinitroparahydroxyphenylphthalide*,  $\text{CO} \begin{smallmatrix} \text{O} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{OH}$   $[(\text{NO}_2)_2 : \text{OH} = 3:5:4]$ , probably, obtained by treating parahydroxy phenylphthalide with the theoretical quantity of nitric acid (sp. gr. = 1.50) in concentrated acetic acid solution, is yellow, and melts at 187°. *Amidoparahydroxyphenylphthalide*,

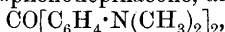


is obtained by reducing the corresponding nitro-compound (Abstr., 1894, i, 600) with tin and hydrochloric acid; it is yellowish, and melts at 229—230°.

When a mixture of phthalaldehydic acid and 1-naphthol is stirred into 73 per cent. sulphuric acid at 0°, the product is 4-hydroxy-naphthylphthalide,  $\text{CO} \begin{smallmatrix} \text{O} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ ; it melts at 222—223°.

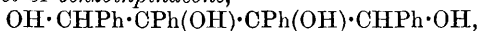
An isomeric substance  $[\text{OH} = 2 \text{ (t)}]$ , obtained in a similar way from 2-naphthol, melts at 234—235°. C. F. B.

**Electrolytic Reduction of Aldehydes and Ketones.** By HUGO KAUFFMANN (*Zeit. Elektrochem.*, 1898, 4, 461. Compare Abstr., 1896, i, 649).—Benzaldehyde, dissolved in alcoholic caustic soda, gives a good yield of the two hydrobenzoins when quickly reduced by means of a fairly large current. Other aldehydes and ketones behave similarly, acetophenone giving acetophenonepinacone, and the ketone,



the corresponding benzhydrol.

In acid solution, the reaction takes place less smoothly, benzaldehyde giving large quantities of resinous products. Benzil (10 grams), dissolved in boiling alcohol (150 c.c.) and 10 per cent. solution of sodium hydroxide (30 c.c.), and electrolysed for 6 hours at 70—80° with 2—3 ampères, gives, besides benzoic and benzilic acids, symmetrical *tetra-phenylerythritol* or *benzoinpinacone*,

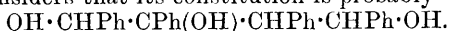


the yield of the latter being about 10 per cent. of the benzil used. This substance melts at about 235°, crystallises from alcohol in slender needles, and is most readily soluble in alcohol containing some alkali, but very sparingly in other solvents. When evaporated, the mother liquor of the benzoinpinacone deposits thick crystals which, after recrystallisation from chloroform, melt at 175° and have the composition  $\text{C}_{28}\text{H}_{26}\text{O}_3$ . Benzoinpinacone was also obtained by the electrolytic reduction of benzoin; when heated at 235—240° in a *vacuum*, it loses  $1\text{H}_2\text{O}$ , forming benzoin. With acetic chloride, it loses water and

forms a diacetyl compound, probably  $\text{O} \begin{smallmatrix} \text{CHPh} \cdot \text{CPh} \cdot \text{OAc} \\ \text{CHPh} \cdot \text{CPh} \cdot \text{OAc} \end{smallmatrix}$ ; this crystallises from alcohol in white plates melting at 198°.

The substance  $\text{C}_{28}\text{H}_{26}\text{O}_3$  does not undergo the pinacone decomposi-

tion ; it forms a monacetyl compound, losing  $1\text{H}_2\text{O}$  at the same time. The author considers that its constitution is probably



T. E.

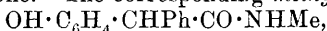
**Condensation of Mandelonitrile with Phenols.** By AUGUSTIN BISTRZYCKI and HUGO SIMONIS (*Ber.*, 1898, **31**, 2812—2813).— $\alpha$ -Hydroxydiphenylacetolactone can be prepared directly from commercial mandelonitrile by acting on the latter with sulphuric acid and phenol, and this greatly lessens the cost of production.

Neither the lactone nor the sodium salt of the acid appears to produce any definite physiological effect on dogs.

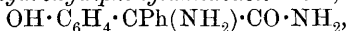
A. H.

**$\gamma$ -Lactones of Phenolic Acids.** By GUSTAV CRAMER (*Ber.*, 1898, **31**, 2813—2821).

I. *Derivatives of Orthohydroxydiphenylacetolactone.*—*Ethyl orthohydroxydiphenylacetate*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{COOEt}$ , obtained by the action of alcoholic hydrogen chloride on the lactone, crystallises in stellate groups of prisms melting at  $104$ — $106^\circ$ .  $\gamma$ -Lactones of alcoholic acids, on the other hand, are usually converted into chloroacids by this treatment. *Orthohydroxydiphenylacetamide* is obtained by the action of ammonia on the lactone, and crystallises in slender needles melting at  $161$ — $162^\circ$ . When it is heated at  $180^\circ$ , it is converted into the lactone. The corresponding *methylamide*,



prepared by the action of methylamine on the lactone, crystallises in small needles melting at  $180$ — $182^\circ$ ; the *anilide*, obtained in a similar manner, crystallises in lustrous, white plates melting at  $143$ — $146^\circ$ . *Orthohydroxydiphenylamidoacetamide*,



is formed by the action of aqueous ammonia on orthohydroxydiphenylbromacetolactone, and melts and decomposes at  $150$ — $151^\circ$ . When it is boiled with hydrochloric acid, it is converted into the *orthohydroxydiphenylglycocine hydrochloride*, which melts at  $275$ — $278^\circ$ . The corresponding *acid* crystallises in very hygroscopic needles melting at  $210$ — $215^\circ$ , and probably has the constitution  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh} \left\langle \begin{smallmatrix} \text{NH}_3 \\ \text{CO} \end{smallmatrix} \right\rangle \text{O}$ .

It follows from this that the additive product obtained by the action of ammonia on the bromolactone is a true hydroxyamide and does not contain the lactone ring. *Orthohydroxydiphenylacetamidacetolactone*,

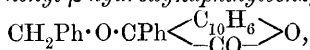
$\text{NHAc} \cdot \text{CPh} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \right\rangle \text{O}$ , obtained by the action of acetic anhydride and sodium acetate on the hydrochloride of orthohydroxydiphenylglycocine, crystallises in slender, lustrous needles melting at  $225$ — $228^\circ$ .

II. *Derivatives of Phenylparacresylacetolactone.*—*Phenylparacresylacetamide*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CHPh} \cdot \text{CO} \cdot \text{NH}_2$ , crystallises in stellate groups of lustrous prisms and melts at  $139$ — $140^\circ$ . *Phenylparacresylbromacetolactone*,  $\text{CPhBr} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \text{CO} \end{smallmatrix} \right\rangle \text{O}$ , forms well developed, tabular monosymmetric crystals [ $a : b : c = 1.8482 : 1 : 2.1060$ ;  $\beta = 85^\circ 13'$ ]. *Phenylparacresylamidoacetamide*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CPh}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH}_2$ , forms lustrous crystals melting at  $146$ — $148^\circ$ . *Phenylparacresylglycocine*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CPh}(\text{NH}_2) \cdot \text{COOH}$ , which is almost insoluble in any of

the ordinary solvents, melts at 190—192°; the *hydrochloride* readily loses hydrogen chloride if left in a desiccator. *Phenylparacresylacetamidoacetolactone*,  $\text{NHAc} \cdot \text{CPh} \langle \text{C}_6\text{H}_3\text{Me} \rangle \text{O}$ , crystallises in lustrous needles melting at 214—216°. *Phenylparacresylethoxyacetolactone*,  $\text{OEt} \cdot \text{CPh} \langle \text{C}_6\text{H}_3\text{Me} \rangle \text{O}$ , crystallises in lustrous prisms melting at 122°. *Phenylparacresylethoxyacetic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CPh}(\text{OEt}) \cdot \text{COOH}$ , crystallises in slender needles melting at 131—134°, and its *amide* in small needles melting at 103—105°.

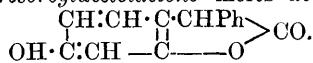
III. *Derivatives of Phenylmetacresylacetolactone*.—*Phenylmetacresylacetamide* crystallises in lustrous prisms melting at 163—166°. *Phenylmetacresylbromacetolactone* forms pale yellow, lustrous plates melting at 96—97°. *Phenylmetacresylethoxyacetolactone* crystallises in lustrous prisms melting at 91—93°. A. H.

**Condensation of Mandelic Acid with  $\beta$ -Naphthol, Resorcinol, and Orcinol.** By HUGO SIMONIS (*Ber.*, 1898, 31, 2821—2830).—Phenyl- $\beta$ -hydroxynaphthylacetolactone is best prepared by the action of mandelonitrile on  $\beta$ -naphthol. The *basic barium salt*,  $\text{C}_{18}\text{H}_{12}\text{O}_3\text{Ba}$ , crystallises with  $3\text{H}_2\text{O}$  in small, soluble prisms, whilst the *normal salt*,  $(\text{C}_{18}\text{H}_{13}\text{O}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , is sparingly soluble, and crystallises in long, thread-like needles. *Phenyl- $\beta$ -hydroxynaphthylbromacetolactone*,  $\text{CPhBr} \langle \text{C}_{10}\text{H}_6 \rangle \text{O}$ , produced by the action of bromine on the lactone, forms well-developed, greenish-yellow, monosymmetric crystals [ $a:b:c = 1.2894:1:0.480$ ;  $\beta = 91^\circ 30'$ ], and melts at 121°. *Phenyl- $\beta$ -hydroxynaphthylmethoxyacetolactone*,  $\text{OMe} \cdot \text{CPh} \langle \text{C}_{10}\text{H}_6 \rangle \text{O}$ , obtained by the action of methylic alcohol on the foregoing compound, crystallises in yellow prisms melting at 136°. *Phenyl- $\beta$ -hydroxynaphthylethoxyacetolactone* forms colourless crystals melting at 145°, and is accompanied by two deep yellow substances melting at 187° and 223° respectively. The corresponding acid forms a *basic barium salt*,  $\text{C}_{20}\text{H}_{16}\text{O}_4\text{Ba}$ , as well as a *normal salt*, both of which are sparingly soluble in water. *Phenyl- $\beta$ -hydroxynaphthylbenzyloxyacetolactone*,



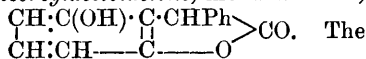
obtained by the action of benzylic alcohol on the bromo-compound, forms colourless crystals and melts at 181°, whilst the corresponding *phenoxy-derivative* melts at 160°.

Mandelic acid reacts with resorcinol in presence of sulphuric acid to form two isomeric lactones. *Phenylresorcyllacetolactone* melts at 133°, and probably has the constitution



It forms tabular asymmetric crystals [ $a:b:c = 0.6007:1:0.7010$ ;  $\alpha = 75^\circ 42'$ ;  $\beta = 116^\circ 19'$ ;  $\gamma = 108^\circ 16'$ ].

The isomeric compound, *isophenylresorcyllacetolactone*, melts at 125°, and probably has the constitution



The crystals belong to the rhombic system [ $a:b:c = 0.895:1:0.784$ ].

Both lactones yield bromo-derivatives, that of the normal lactone melting at  $145^{\circ}$ , and that of the isolactone at  $142^{\circ}$ . *Dibromophenyl-resorcyllactone*,  $C_{14}H_8O_3Br_2$ , is obtained from the lactone melting at  $183^{\circ}$ , and probably has the constitution  $CO \langle \text{CPhBr} \rangle \text{O} \text{---} C_6H_2Br \cdot OH$ .

Orcinol, like resorcinol, yields two isomeric lactones. *Phenylorcyllactone* crystallises in slender needles melting at  $155^{\circ}$ . The *isolactone* melts at  $172^{\circ}$ . *Monobromophenylorcyllactone* forms brownish crystals melting at  $185^{\circ}$ , whilst the *dibromo-lactone* melts at  $205^{\circ}$ .

A. H.

**A Periodide of Triphenylbromomethane.** By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1898, 20, 790).—On mixing solutions, in benzene or carbon bisulphide, of triphenylbromomethane and excess of iodine, a *periodide*,  $CPh_3BrI_4$ , crystallises out; after recrystallisation from benzene or carbon bisulphide, it melts at  $121$ — $122^{\circ}$ . The periodide may be obtained in bluish-green, iridescent, hexagonal prisms or in small needles. On two occasions, the unusual phenomenon of the formation of hollow crystals was observed, the canal apparently coinciding with the longitudinal axis of the crystal. The author points out that all periodides hitherto described are those of metallic salts or of bases, whereas triphenylbromomethane is not a base.

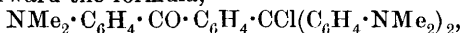
G. W. F. H.

**Tetraphenylmethane.** By MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1898, 20, 773—780).—This paper is a revision of the author's work on tetraphenylmethane (*Abstr.*, 1897, i, 623). Triphenylmethane is brominated, and the triphenylbromomethane produced treated with phenylhydrazine, when it yields triphenylmethanehydrazobenzene; this, when oxidised with nitrous anhydride, gave triphenylmethane-azobenzene melting at  $110$ — $112^{\circ}$ , which, on heating at  $110$ — $120^{\circ}$ , evolves nitrogen, forming tetraphenylmethane, the yield being, however, very poor. Tetraphenylmethane crystallises from benzene in white, glistening needles.

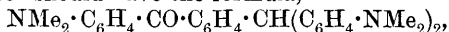
That tetraphenylmethane is really formed, is indicated, not only by the analysis, but by a cryoscopic determination of the molecular weight; moreover, the substance is readily and completely converted into a tetranitro-derivative melting at  $275^{\circ}$ ; this does not yield a sodium derivative by the action of sodium ethoxide, whereas the nitrophenylmethane derivatives,  $CH_2[C_6H_3(NO_2)_2]_2$ ,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CN$ ,  $CH(C_6H_4 \cdot NO_2)_3$ , which still contain hydrogen attached to the methane carbon atom, readily yield sodium derivatives. Tetranitrotetraphenylmethane appears to be reduced by zinc dust and acetic acid to leucoparosaniline.

G. W. F. H.

**Constitution of Phthalyl-Green.** By ALBIN HALLER and ALFRED GUYOT (*Compt. rend.*, 1897, 125, 1153—1156. Compare *Abstr.*, 1881, 587, and 1898, i, 483). The colouring matter produced by the condensation of phthalyl tetrachloride and dimethylaniline is identical with O. Fischer's phthalyl-green. There are many points of resemblance between this compound and malachite-green, and the authors put forward the formula,



as being most in accordance with the reactions of the former substance; in other words, phthalyl-green is malachite-green containing the radicle,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}$ , introduced into an ortho-position in the non-substituted phenyl group. The leuco-base obtained from such a colouring matter should have the formula,



which is in agreement with O. Fischer's analytical results. Rosenstiehl has shown that the basic colouring matters of the triphenylmethane series containing  $n$  atoms of amidic nitrogen are capable of combining with  $(n + 1)$  molecules of hydrochloric acid to form polyhydrochlorides, of which pararosaniline tetrahydrochloride,  $\text{Cl}(\text{C}_6\text{H}_4 \cdot \text{NH}_2, \text{HCl})_3$ , may be taken as the type.

Phthalyl-green behaves like pararosaniline, and forms a tetrahydrochloride. This compound, although containing four chlorine atoms ought not to combine with 2 molecules of platinic chloride, since the formation of a platinochloride is due only to the presence of quinquevalent nitrogen atoms. It might be expected, however, that 2 molecules of the tetrahydrochloride would combine with 3 molecules of platinic chloride. The platinochloride obtained by the addition of platinic chloride to a solution of the colouring matter in concentrated hydrochloric acid has the formula  $(\text{C}_{32}\text{H}_{34}\text{N}_3\text{OCl})_2 \cdot 3\text{H}_2\text{PtCl}_6$ . G. T. M.

**Mercurial Compounds of  $\beta$ -Naphthol.** By EUGEN BAMBERGER *Ber.*, 1898, 31, 2624—2626).—The author has obtained with  $\beta$ -naphthol results similar to those described by Dimroth (this vol., i, 54) in the case of phenol.  $\beta$ -Hydroxynaphthyl-1-mercuric acetate,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{Hg} \cdot \text{OAc}$ , is made by adding  $\beta$ -naphthol (13.2 grams) to a clear solution of mercuric oxide (20 grams) in hot acetic acid (520 c.c.); it separates at once as a heavy, crystalline precipitate, and can be purified by recrystallisation from hot acetic acid. It crystallises in white, shining needles, and, when quickly heated, melts and decomposes at  $185^\circ$ ; it is sparingly soluble in most of the usual media, but dissolves readily in soda, and is reprecipitated on addition of acetic acid; on addition of ammonium sulphide to its aqueous solution, a voluminous, yellow precipitate is produced which blackens when the liquid is heated, mercuric sulphide being formed. The mercury is very loosely attached to the naphthol nucleus, and the union is destroyed by the addition of soda or of diazotates,  $\beta$ -naphthol being formed in the first case, and phenolazonaphthols being produced in the second.

A. L.

**Synthetical Isoborneols; their Identity with the Fenchylic Alcohols.** By GUSTAVE BOUCHARDAT and J. LAFONT (*Compt. rend.*, 1898, 126, 755—757).—Synthetically prepared dextrorotatory isoborneol, obtained by the authors by the action of certain acids on lævorotatory turpentine, consists of a mixture of the dextrorotatory and inactive fenchylic alcohols; these, on oxidation, give rise to lævorotatory and inactive fenchone respectively. The former is the optical antipode of the dextrorotatory fenchone obtained from oil of fennel; both compounds have the same crystalline form and melting point, and their specific rotations are equal in magnitude but opposite in sign. The corresponding fenchone oximes bear similar relations to

each other, and when equal weights of them are mixed together, in ethereal solution, a racemoid form, melting at 154—156°, is obtained on evaporation. When lævorotatory fenchone is reconverted into dextrorotatory fenchylic alcohol by reduction with alcoholic potash or sodium and alcohol, the optical activity of the substance is less than it was originally. G. T. M.

**Beetroot-resin Acid.** By KARL ANDRLÍK and EMIL VOTOCEK (*Chem. Centr.*, 1898, i, 621—622; from *Neu. Zeit. Rüb.-Zuck.-Ind.*, 40, 39—44).—According to the authors, the substance obtained from the scum formed in the first treatment of the sugar liquors with lime and carbonic anhydride is not ischolesterol, as Kollrepp supposed, but a kind of resin to which they give the name beetroot-resin acid. It is prepared by treating the scum with dilute hydrochloric acid and extracting the dry, insoluble material with alcohol. The scum on the waste water of the factory, the deposits in the heating apparatus for the diffusion process, and the diffused juice also contain this substance. It crystallises from alcohol in colourless, silky needles, melts at 299—300°, has a specific rotatory power  $[\alpha]_D = +74.4^\circ$  at 20°, is insoluble in water, easily soluble in boiling alcohol, amyl alcohol, and isobutylic alcohol, and less soluble in methylic than in ethylic alcohol. It dissolves easily in glacial acetic acid, but the solution, on evaporation, does not yield the original compound. When heated above the melting point, it sublimes and partially decomposes, forming a liquid and a crystalline sublimate; the latter melts and chars at 241°. The resin-acid has the composition  $C_{22}H_{36}O_2$ , and crystallises with  $1H_2O$ . The colour reactions with sulphuric acid and acetic anhydride are like those of abietic acid, vitine, ursone, gentiol, cholesterol, and many resin-acids. The sodium and potassium salts were prepared. E. W. W.

**Aloins.** By EUGÈNE LÉGER (*Compt. rend.*, 1898, 127, 234—236. Compare *Abstr.*, 1898, i, 445).—*Trichlorobarbaloin*,  $C_{16}H_{13}Cl_3O_7 + H_2O$ , obtained by the action of potassium chlorate on a solution of barbaloin in concentrated hydrochloric acid, crystallises from alcohol of 90 per cent. in monoclinic, rhomboidal tablets  $[a:b:c = 1.5448:1:1.3880]$ . Unlike barbaloin, it dissolves in sodium carbonate solution, but it does not displace carbonic acid. When heated in sealed tubes with acid chlorides, it yields *triacetyltrichlorobarbaloin*, which crystallises in very thin, microscopic, rhomboidal lamellæ, and *tribenzoyltrichlorobarbaloin*, an amorphous compound very soluble in acetone, but almost insoluble in alcohol. Under different conditions, barbaloin itself yields only a diacetyl or dibenzoyl derivative, but there can be no doubt that barbaloin contains three hydroxyl groups, which have a phenolic function, for it gives an olive-green coloration with ferric chloride, dissolves in alkali hydroxides, but not in the carbonates, and when heated with sodium hypobromite in excess, yields carbonic and oxalic acids and carbon tetrachloride.

*Isobarbaloin*,  $C_{16}H_{16}O_7$ , is found in the last fractions of the crystallisation of a mixture of aloins. It crystallises from methylic alcohol in opaque nodules, composed of elongated and truncated, micro-

scopic lamellæ which contain  $3\text{H}_2\text{O}$  and are efflorescent; when crystallised from water, it forms pale yellow, prismatic needles which contain  $2\text{H}_2\text{O}$ . With benzoic chloride in presence of pyridine, it yields *dibenzoylisobarbaloin*, very similar to the corresponding barbaloin derivative. *Trichlorisobarbaloin*, obtained by the action of potassium chlorate and hydrochloric acid, forms brilliant yellow, prismatic needles; when heated in sealed tubes with acetic chloride, it yields a crystallisable triacetyltrichlorisobarbaloin. *Tribromisobarbaloin* is identical with the compound hitherto described as tribromobarbaloin.

The relative proportions of barbaloin and isobarbaloin vary greatly in aloes from different localities.  
C. H. B.

**Kosin.** By GIROLAMO DACCAMO and GIOVANNI MALAGNINI (*L'Orosi*, 1897, 20, 361—371).—Commercial kosin, obtained from the flowers of *Hagenia abyssinica*, melts at  $147\text{--}149.5^\circ$ , and appears to be a mixture of at least two substances, since, on fractional dissolution in, and crystallisation from, alcohol, it yields products having melting points ranging from  $105^\circ$  to  $161^\circ$ . The portion of highest melting point is the principal constituent of the commercial substance, and resembles in its properties the kosin described by Flückiger and Buri; it crystallises in long, yellow needles, which are insoluble in water but more or less soluble in organic solvents, and dissolves in alkalis, yielding solutions from which it is reprecipitated unchanged on the addition of acids. Its solutions give a violet coloration with ferric chloride, reduce an ammoniacal solution of silver nitrate, and react with phenylhydrazine to form resinous products, and probably a hydrazone; no reaction takes place, however, with Fehling's solution or with hydroxylamine. This substance, to which the term "kosin" is properly restricted, is shown by analysis and by cryoscopic molecular weight determinations (found, 411; theory, 402) to be more accurately represented by the formula  $\text{C}_{22}\text{H}_{26}\text{O}_7$ , than by the formula  $\text{C}_{31}\text{H}_{38}\text{O}_{10}$ , proposed by Flückiger and Buri.

Triacetylkosin,  $\text{C}_{22}\text{H}_{23}\text{Ac}_3\text{O}_7$ , obtained by the action of acetic anhydride on kosin, crystallises from alcohol in small, colourless needles. The corresponding *benzoyl* derivative, obtained by the action of benzoic chloride on a solution of kosin in caustic potash, forms small, almost colourless crystals. The analyses of these compounds and cryoscopic molecular weight determinations are in accordance with the formula proposed for kosin by the authors.

Kosin readily undergoes oxidation in alkaline solution, with the formation of isobutyric acid and complex resinous substances. With potassium permanganate, oxalic acid is also obtained, whilst when bromine or iodine is employed, bromoform and iodoform are respectively produced. Kosin resembles filicic acid in many respects, but differs from it in not reacting with Fehling's solution or with hydroxylamine. The existence of three hydroxyl groups in the molecule of kosin is shown by the formation of the acetyl and benzoyl derivatives, whilst its behaviour with phenylhydrazine and with oxidising agents indicates the presence of a ketonic nucleus to which an isopropyl group is probably attached.  
N. L.



**Strophanthin.** By LEOPOLD KOHN and VICTOR KULISCH (*Monatsh.*, 1898, 19, 385—402. Compare Abstr., 1898, i, 326 and 327).—The strophanthin which the authors have described (Abstr., 1898, i, 329) is not identical with Feist's preparation (*ibid.*). The seeds from which they obtained the principle were those of *Strophanthus Kombé* or *S. hispidus*, probably the former, as they appear to be identical with those employed by Feist, and the isolation of the substance was achieved by Arnaud's process (Abstr., 1888, 1310).

The seeds, carefully freed from the adherent hairs, were powdered as finely as possible, washed in a Soxhlet's apparatus with light petroleum, and extracted with 70 per cent. alcohol. To the alcoholic extract, basic lead acetate and lead hydroxide were added, the lead being subsequently eliminated from the filtered liquid by means of hydrogen sulphide; the filtrate was then evaporated in a vacuum, and the crude strophanthin so obtained purified by repeated crystallisation from water; it appears to be identical with Merck's "crystallised strophanthin," which is obtained from *Strophanthus hispidus*.

The substance is inactive; it is very hygroscopic and, when damp, melts at 100°; the melting point of the anhydrous substance is very uncertain, but lies near 179°.

The authors' analyses gave numbers in close agreement with those obtained by Arnaud, but it is as yet uncertain which of the formulæ,  $C_{31}H_{48}O_{12}$  or  $C_{38}H_{58}O_{15}$ , represent the true composition of the substance.

Strophanthin appears to contain a methoxy-group; a determination by Zeisel's method gave a methoxyl content = 3·77—3·4 per cent., a number which points to the second of the above formulæ as being the correct one.

**Acetylstrophanthin**,  $C_{31}H_{44}O_8(OAc)_4$ , or  $C_{38}H_{53}O_{10}(OAc)_5$ , is made by heating strophanthin with acetic anhydride and anhydrous sodium acetate, and can be purified by recrystallisation from hot alcohol; it forms very long, slender, colourless microscopic needles, melts at 236—238°, and is insoluble in water.

Strophanthidin crystallises from hot alcohol in beautiful, slender, white needles which aggregate to form silky leaflets. It melts at 195°, does not dissolve in water, but is very hygroscopic; it cannot be dried at 100°, as it suffers slight decomposition at that temperature. It has the formula  $C_{19}H_{28}O_4$ , or  $C_{28}H_{40}O_6$ , but, like strophanthin, its methoxyl content is too low, and is lower even than that required by the latter formula.

A. L.

**Action of Cinnamaldehyde on Phenyltoluidoacetonitrile.** By WILHELM VON MILLER and JOSEF PLÖCHL (*Ber.*, 1898, 31, 2718—2720).—In distinction from the behaviour of aromatic aldehydes, which yield two indifferent isomeric compounds with anilido-derivatives or with amido-nitriles, aliphatic aldehydes yield but one indifferent product (compare this vol., i, 127). In order to examine the behaviour of unsaturated aldehydes under similar conditions, the action of cinnamaldehyde on phenyltoluidoacetonitrile has been studied.

*Diphenyltolylpyrrolone*,  $\begin{matrix} CH:CPh \\ CH:CPh \end{matrix} > N \cdot C_6H_4Me$ , obtained by heating

phenyltoluidoacetonitrile with cinnamaldehyde and potash in alcohol, crystallises from alcohol in lustrous prisms, and melts at  $181^{\circ}$ ; it arises from the union of the aldehyde and nitrile in molecular proportion, involving elimination of water and hydrogen cyanide, also in molecular proportion. The additive compound,  $\text{CHPh}:\text{CH}:\text{CH}(\text{OH})\cdot\text{CPh}(\text{CN})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , melts and decomposes at  $175^{\circ}$ ; it doubtless represents an intermediate stage in the production of diphenyltolylpyrroline, which is generated along with hydrogen cyanide when the substance is heated.

M. O. F.

**Distillation of Mixtures of Pyridine and Aliphatic Acids.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1897, 125, 1187—1189).—Chemical combination evidently occurs when formic, acetic, and propionic acids are mixed with pyridine, for an appreciable amount of heat is developed, but when the mixture is titrated with standard baryta, using turmeric or phenolphthalein as indicators, the acidity is found to be equal to the whole amount of acid added. After six fractionations of a mixture of propionic acid and pyridine, in molecular proportion, a distillate is obtained boiling at  $150\text{--}151^{\circ}$  under a pressure of 760 mm. This liquid has approximately the composition  $2\text{C}_3\text{H}_6\text{O}_2, \text{C}_5\text{H}_5\text{N}$ , and it boils  $11^{\circ}$  higher than propionic acid and  $37^{\circ}$  higher than pyridine. When boiled under reduced pressure, the mixture has no definite boiling point, and the first distillates contain more pyridine than is required by the above formula.

A mixture of acetic acid and pyridine behaves in a similar manner; the least volatile portion boils at  $139\text{--}140^{\circ}$  under 760 mm., and its composition corresponds with  $3\text{C}_2\text{H}_4\text{O}_2, 2\text{C}_5\text{H}_5\text{N}$ . When fractionated, this portion is gradually dissociated; ebullition always commences at  $100^{\circ}$ , and the temperature rises slowly to  $139\text{--}140^{\circ}$ ; when distilled under a pressure of 60 mm., it passes over unchanged at  $74^{\circ}$ , but under 20 mm. it is dissociated.

A mixture of pyridine and formic acid, in molecular proportion, after seven fractionations, yields a distillate boiling at  $148\text{--}151^{\circ}$  (760 mm.), of the composition  $5\text{CH}_2\text{O}_2, 2\text{C}_5\text{H}_5\text{N}$ ; this mixture, when distilled under a pressure of 36 mm., boils at  $74^{\circ}$  without dissociation.

G. T. M.

**Ammonio- and Pyridine Salts and Hydrates of Bivalent Metals.** By FRITZ REITZENSTEIN (*Zeit. anorg. Chem.*, 1898, 18, 253—304. Compare Abstr., 1895, i, 121; 1897, i, 380).—The author discusses the relations between the ammonium salts, hydrates, and pyridine compounds of metals. The repeated occurrence of the same type in the three series is most easily explained by Werner's theory. The character of the acid residue which is combined with the metal becomes of more importance as the number of pyridine molecules increases; and the influence of the metallic atom varies in the inverse manner. The greatest number of pyridine molecules which can be combined is six, and this occurs in the compounds with  $\text{CuBr}_2$ ,  $\text{CdBr}_2$ , and  $\text{CdI}_2$ . The greatest number of quinoline molecules is four, occurring in the compounds with  $\text{CuCl}_2$  and  $\text{CoCl}_2$ . Isomerides of the

formula  $\text{=MeX}_2\text{2Py}$ , which, according to Jörgensen's and Werner's theories, are possible, have not been obtained.

The author gives a table of all the known ammonium, pyridine, and quinoline salts and hydrates, and describes the following new compounds.

*Monopyridine nickel chloride pentahydrate*,  $\text{NiCl}_2\cdot\text{C}_5\text{H}_5\text{N}\cdot 5\text{H}_2\text{O}$ , is obtained by exposing monopyridine nickel chloride to the air for 4–5 days.

*Nickel chloride monopyridine hydrochloride*,  $\text{NiCl}_2\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ , is obtained by treating finely divided nickel chloride with pyridine, dissolving the product in concentrated hydrochloric acid, and evaporating the solution on the water-bath. It crystallises in flesh-coloured needles, deliquesces in the air, gives a green solution in water, and characteristic precipitates with potassium ferrocyanide and ferricyanide. When the mother liquors obtained in the preparation of this salt are evaporated, a compound is obtained which separates in blue crystals, and is probably a tetrahydrochloride compound.

*Nickel chloride dipyridine hydrochloride*,  $\text{NiCl}_2\cdot(\text{C}_5\text{H}_5\text{N}\cdot\text{HCl})_2$ , was obtained on one occasion by dissolving nickel oxide in pyridine hydrochloride, and concentrating the solution on the water-bath, but the author was unable to obtain it again. The solution, on evaporation, first yields the salt  $2\text{NiCl}_2\cdot 3\text{C}_5\text{H}_5\text{N}$ , crystallising in greenish-yellow needles; on further concentration, it yields  $\text{NiCl}_2\cdot\text{C}_5\text{H}_5\text{N}$ , then  $\text{NiCl}_2\cdot\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ , and finally  $\text{NiCl}_2\cdot 4\text{C}_5\text{H}_5\text{N}$ , which crystallises from pyridine in bright blue needles.

*Nickel sulphate tripyridine dihydrate*,  $\text{NiSO}_4\cdot 3\text{C}_5\text{H}_5\text{N}\cdot 2\text{H}_2\text{O}$ , obtained by adding excess of pyridine to an aqueous solution of nickel sulphate, then adding alcohol and boiling, is a bluish-green, crystalline mass soluble in water, and gives a green precipitate with potassium ferrocyanide.

Cobalt chloride tetrapyridine,  $\text{CoCl}_2\cdot 4\text{C}_5\text{H}_5\text{N}$ , is obtained by heating a mixture of cobalt chloride and excess of pyridine hydrochloride in alcoholic solution; when dissolved in alcohol, it yields a blue compound, probably  $\text{CoCl}_2\cdot 2\text{C}_5\text{H}_5\text{N}\cdot 2\text{EtOH}$ , which quickly decomposes into the dipyridine compound.

*Cobalt chloride monopyridine pentahydrate*,  $\text{CoCl}_2\cdot\text{C}_5\text{H}_5\text{N}\cdot 5\text{H}_2\text{O}$ , is obtained as a reddish, crystalline mass by allowing cobalt chloride monopyridine to remain exposed to the air for a few days.

*Dicobalt chloride pentapyridine hydrochloride*,  $2\text{CoCl}_2\cdot(\text{C}_5\text{H}_5\text{N}\cdot\text{HCl})_5$ , obtained by heating the tetrapyridine compound dissolved in water with excess of hydrochloric acid, and also by the action of concentrated hydrochloric acid on a mixture of cobalt chloride and pyridine, is a dark blue, crystalline powder, and gives a red solution in water; when treated with silver nitrate, all the chlorine is precipitated.

*Cobalt chloride dipyridine monohydrochloride*,  $\text{CoCl}_2\cdot 2\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ , obtained by treating the preceding compound in alcoholic solution with the theoretical quantity of silver oxide, crystallises in dark blue crystals, melts at  $155^\circ$ , is soluble in cold water with a red coloration, and, when heated in the air-bath at  $150^\circ$  is converted into the basic chloride,  $\text{CoCl}_2\cdot\text{CoO}$ . When treated with excess of silver oxide in alcoholic solution, it is converted into cobalt chloride dipyridine.

When cobalt chloride dipyridine is treated with ammonia and hydrochloric acid, a *salt* of the composition  $\text{CoCl}_2 \cdot (\text{C}_5\text{H}_5\text{NCl}, \text{NH}_4\text{Cl})_2 \cdot 3\text{H}_2\text{O}$ , is obtained, which crystallises from absolute alcohol in bright blue needles, darkens at  $120^\circ$ , melts at  $128\text{--}130^\circ$ , and when exposed to the air quickly turns red. The tetrapyridine and dipyridine compounds of cobalt chloride, when exposed to the air, take up water and give off pyridine in varying proportions according to the time of exposure, and compounds of the following composition were obtained,  $\text{CoCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ ;  $\text{CoCl}_2 \cdot 1\frac{1}{2}\text{C}_5\text{H}_5\text{N} \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , and  $\text{CoCl}_2 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot 3\text{H}_2\text{O}$ .

*Cobalt sulphate tripyridine dihydrate*,  $\text{CoSO}_4 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ , obtained by treating an aqueous solution of cobalt sulphate with pyridine, separates in blood-red crystals, cannot be recrystallised from absolute alcohol or pyridine, is decomposed by warm water with precipitation of cobalt hydroxide, and, when treated with barium chloride, gives a quantitative precipitate of barium sulphate. When allowed to remain exposed to the air for a month, it is converted into the compound  $\text{CoSO}_4 \cdot \text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ .

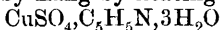
Cobalt nitrate, when heated with pyridine, yields a red compound, which can be recrystallised from absolute alcohol, smells strongly of pyridine, and is probably  $\text{Co}(\text{NO}_3)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ .

The author was unable to obtain a compound of ferrous chloride with pyridine in aqueous solution. When solid ferrous chloride is shaken with pyridine, the compound  $\text{FeCl}_2 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$  is obtained; this is a yellow, crystalline powder, has a strong odour of pyridine, is very easily decomposed, and is slightly soluble in water.

*Ferrous sulphate tripyridine dihydrate*,  $\text{FeSO}_4 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ , obtained in brownish-yellow crystals by adding pyridine to an aqueous solution of ferrous sulphate, has a strong odour of pyridine, is easily decomposed with the formation of basic salts, and, with barium chloride, gives the theoretical quantity of barium sulphate.

*Cadmium sulphate tripyridine dihydrate*,  $\text{CdSO}_4 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ , obtained in a similar manner to the preceding compound, is a white, crystalline precipitate, soluble in water. When heated at  $120^\circ$  for 1 hour, or allowed to remain 35 days exposed to the air, the pyridine is eliminated and  $\text{CdSO}_4 \cdot 2\text{H}_2\text{O}$  remains.

When anhydrous copper sulphate is treated with pyridine, a dark blue, crystalline powder is obtained, which is probably  $2\text{CuSO}_4 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$ . It is very unstable, and cannot be obtained in a pure state. It is partially soluble in water with the formation of a basic salt, insoluble in pyridine, and when boiled with absolute alcohol is converted into a green powder. When allowed to remain exposed to the air, it becomes bluish-green, and thus has the composition  $2\text{CuSO}_4 \cdot \text{C}_5\text{H}_5\text{N} \cdot 4\text{H}_2\text{O}$ . The compound,  $2\text{CuSO}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$ , obtained by digesting anhydrous copper sulphate with absolute alcohol and excess of pyridine for some time, is a bright blue powder, which, when boiled with absolute alcohol, is converted into the compound  $\text{CuSO}_4 \cdot \text{C}_5\text{H}_5\text{N}$ , identical with the pyridine copper sulphate obtained by Jørgensen by heating copper dipyridine sulphate, and by Lang by heating the compound



at  $110^\circ$ .

*Lead chloride pyridine*,  $\text{PbCl}_2 \cdot \text{C}_5\text{H}_5\text{N}$ , obtained by boiling lead peroxide with a solution of pyridine hydrochloride in hydrochloric acid, crystallises quickly from the filtered solution in beautiful, white crystals.

*Manganese tetrachloride dipyridine*,  $\text{MnCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ , is obtained by warming freshly precipitated manganese dioxide with pyridine hydrochloride dissolved in hydrochloric acid. On concentrating the filtrate on the water-bath, it separates in large, bright green crystals, which give a colourless solution with water; when allowed to remain exposed to the air, it loses chlorine and is converted into the compound  $\text{MnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .

*Manganous chloride dipyridine*,  $\text{MnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , obtained by adding excess of pyridine to a concentrated solution of manganous chloride, separates in brown crystals which darken on exposure, is easily soluble in warm water, and when heated at  $160\text{--}165^\circ$  is converted into the compound  $\text{MnCl}_2 \cdot 1\frac{1}{2}\text{C}_5\text{H}_5\text{N}$ .

*Manganous chloride diquinoline*,  $\text{MnCl}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$ , obtained by adding excess of quinoline to an alcoholic solution of manganous chloride, separates in brown crystals, is insoluble in cold water, dissolves in hot water with decomposition, and is soluble in cold alcohol.

*Cadmium bromide diquinoline*,  $\text{CdBr}_2 \cdot 2\text{C}_9\text{H}_7\text{N}$ , obtained by boiling cadmium bromide with excess of quinoline, separates from absolute alcohol in white prisms, and is sparingly soluble in cold water.

E. C. R.

**Pyridine Compounds of Quadrivalent Palladium.**—By ARTHUR ROSENHEIM and THEODOR A. MAASS (*Zeit. anorg. Chem.*, 1898, 18, 331—338).—Amine bases of quadrivalent palladium have not yet been obtained. The dipalladamine chloride,  $\text{Pd}_2\text{Cl}_2(\text{NH}_3\text{Cl})_4$ , described by Deville and Debray (*Compt. rend.*, 86, 926) is a mixture consisting for the most part of ammonium palladium chloride  $(\text{NH}_4)_2\text{PdCl}_6$ , and this is the only compound which the authors were able to isolate by the action of chlorine water on palladosamine chloride in the cold. By the action of chlorine water at higher temperatures, ammonium palladious chloride,  $(\text{NH}_4)_2\text{PdCl}_4$ , is formed, with evolution of nitrogen. The action of bromine on palladosamine chloride takes place in a similar manner. The pyridine bases of quadrivalent palladium are, however, easily obtained.

*Palladodipyridine chloride*,  $\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ , is obtained by adding pyridine to a solution of palladious chloride; a red precipitate is obtained which dissolves when boiled with excess of pyridine, and on adding strong hydrochloric acid, palladodipyridine chloride is precipitated as a bright yellow, crystalline powder.

*Palladidipyridine chloride*,  $\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$  obtained by the action of chlorine on the preceding compound suspended in chloroform, crystallises in small, dull, orange prisms, gives off chlorine when exposed to damp air, and is fairly stable in dry air; when heated with potassium hydroxide, a brown precipitate of palladium hydroxide is obtained, and when the cold product is carefully neutralised with hydrochloric acid, potassium palladichloride,  $\text{K}_2\text{PdCl}_6$ , crystallises out in characteristic cherry-red octahedra. When shaken with an

aqueous solution of potassium iodide, two atoms of chlorine are eliminated, and palladodipyridine chloride is formed.

*Palladidipyridine dibromochloride*,  $\text{Pd}(\text{C}_5\text{H}_5\text{NBr}_2)_2\text{Br}_2\text{Cl}_2$ , obtained by shaking palladodipyridine chloride suspended in chloroform with bromine, is a deep orange-red, crystalline powder, and is much less stable than the preceding compound. When boiled with potassium hydroxide and then neutralised, potassium palladichloride is obtained. The authors were unable to obtain a similar compound by the action of bromine on palladodipyridine bromide.

*Palladidipyridine di-iodochloride*,  $\text{Pd}(\text{C}_5\text{H}_5\text{N})_2\text{I}_2\text{Cl}_2$ , obtained in a similar manner to the preceding compounds, crystallises in brown needles, and is remarkably stable on exposure to the air. When boiled with water or with potassium hydroxide, it is completely decomposed, with the formation of black palladous iodide. When, however, it is shaken with pure carbon bisulphide, it gives off two atoms of iodine, and is quantitatively converted into palladodipyridine chloride.

E. C. R.

**Derivatives of Nicotinic Acid.** By AMÉ PICTET and G. SUSSDORFF (*Chem. Centr.*, 1898, i, 677—678; from *Arch. Sci. phys. nat. Genève*, [iv], 5, 113—128).—An 82 per cent. yield of nicotinic acid is obtained by pouring a solution of 10 grams of nicotine in 100 c.c. of water and 20 grams of concentrated nitric acid into 250 grams of concentrated nitric acid, and heating the mixture on the water-bath until no more red fumes are evolved; the *nitrate* of the acid, which is obtained on evaporation, melts at  $185^\circ$ . Nicotinic acid, prepared from the nitrate by means of the copper compound or by heating with acetic anhydride or by distilling alone, crystallises in white needles and melts at  $229^\circ$ . *Ethyl nicotinate*, obtained by treating the acid with alcohol and hydrochloric acid, boils at  $220$ — $221^\circ$  under a pressure of 724 mm.; the nitrate melts at  $185^\circ$ , and the hydrochloride at  $126$ — $127^\circ$ . By the action of fatty amines on ethyl nicotinate, the following amides were prepared. *Methylnicotinamide*,  $\text{C}_5\text{NH}_4\cdot\text{CO}\cdot\text{NHMe}$ , crystallises from chloroform in long needles and melts at  $104$ — $105^\circ$ ; the *methiodide*,  $\text{C}_7\text{H}_8\text{NO}_2\cdot\text{MeI}$ , crystallises in needles, melts at  $174^\circ$ , and with silver nitrate forms the corresponding nitrate which crystallises from a mixture of alcohol and ether in prisms, and melts at  $155$ — $156^\circ$ . By treating methylnicotinamide methiodide with silver oxide, an aqueous solution of the hydroxide is obtained, which, on evaporation, decomposes into methylamine and trigonellin. *Amylnicotinamide* boils at  $191$ — $193^\circ$  under a pressure of 8 mm., and is easily soluble in ether. *Allylnicotinamide* boils at  $186$ — $189^\circ$  under a pressure of 8 mm., at  $315$ — $316^\circ$  under the ordinary pressure, and cannot be purified by distillation. By preparing the chloride by acting on nicotinic acid with phosphorus pentachloride, removing the phosphorus oxychloride, and then treating the residue with aromatic amines, hydrochlorides of substituted aromatic amides are obtained, and these, with sodium carbonate, yield the free amides. *Nicotinamile*,  $\text{C}_5\text{NH}_4\cdot\text{CO}\cdot\text{NHPh}$ , crystallises from water in needles containing  $2\text{H}_2\text{O}$  and melts at  $85^\circ$ ; the anhydrous compound crystallises from a mixture of light petroleum and benzene or light petroleum and chloro-

form in needles and melts at  $132^{\circ}$ . *Nicotinoparatoluidide* crystallises from water in needles and melts at  $150^{\circ}$ . Attempts to introduce a methyl group into allylnicotinamide failed, but potassium-methylnicotinamide and allylic iodide yield *methylallylnicotinamide* as a viscous liquid. Attempts to remove water from the latter compound, and to obtain nicotyrine from methylnicotinamide and allylic alcohol at  $160$ — $170^{\circ}$  also failed.

- *Piperidine nicotinate*,  $C_5NH_4 \cdot COOH, C_5NH_{11}$ , crystallises in long, colourless needles and melts at  $122^{\circ}$ . E. W. W.

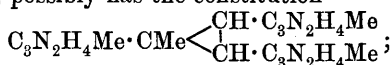
**Transformation of Fatty Ketazines and Aldazines into Pyrazoline Derivatives.** By THEODOR CURTIUS and ED. ZINKEISEN *J. pr. Chem.*, 1898, [ii], 58, 310—332. Compare Abstr., 1894, i, 348).

—Maleates of pyrazolines,  $NH < \begin{matrix} N=CR \\ CRMe \cdot CH_2 \end{matrix}$  [ $R:R:Me = 3:5:5$ ], are obtained by treating ketazines,  $CRMe:N:N:CRMe$  (Abstr., 1891, 1355), with maleic acid, sometimes in alcoholic solution, and purifying the product by dissolving it in alcohol and precipitating it with ether; the free base is obtained by treating this product with potash. Only ketazines which contain at least one methyl group,  $>C:N:N:CRMe$ , are capable of reacting in this way; diethylketazine,  $CEt_3:N:N:CEt_3$ , for example, will not do so. The pyrazoline derivatives obtained distil without decomposition under diminished pressure; the boiling point and index of refraction increase with the molecular weight, whereas the specific gravity decreases. They are stable in the presence of acids, yielding no hydrazine salt, even on boiling, but potassium permanganate oxidises them readily, the molecule being completely broken up. They are not coloured by oxidising agents in dilute solution (Knorr's pyrazoline reaction; probably only given by derivatives in which the  $NH$ -group has become  $NPh$ ). Of the compounds described, only 5-methylpyrazoline resembles pyrazoline itself (Abstr., 1895, i, 248) in other respects; the rest do not form azo-dyes, they are not coloured yellow by nitrous acid, they do not colour a pine splint yellow, and they are not oxidised to pyrazoles by bromine.

3:5:5-Trimethylpyrazoline boils at  $57$ — $59^{\circ}$  under 14 mm. pressure; sp. gr. = 0.903 at  $18^{\circ}$ , 0.907 at  $10^{\circ}$ ; index of refraction  $n_D = 1.46149$  at  $10^{\circ}$ ; when oxidised with dilute permanganate nitrogen, carbonic anhydride and pyruvic acid are formed; when treated with bromine in chloroform solution, its own *hydrobromide*, which melts at  $171^{\circ}$ , is the product. 5-Methyl-3:5-diethylpyrazoline boils at  $90$ — $93^{\circ}$  under 20 mm., at  $78$ — $80^{\circ}$  under 14 mm. pressure; sp. gr. = 0.898 at  $18^{\circ}$ ; the hydrochloride, platinochloride, picrate, methiodide, and benzoyl derivatives are oils which would not crystallise; with bromine, an oily product was obtained that was not the hydrobromide; in the air, this pyrazoline evolves nitrogen, and yields a substance,  $C_8H_{14}O$ , boiling at  $157$ — $158^{\circ}$ , which forms an oily compound with phenylhydrazine, and decolorises an ethereal solution of bromine, and so is probably  $CEtO \cdot CH:CRMeEt$ , a homologue of mesitylic oxide, although it does not, like the latter, condense with hydrazine; this substance is also obtained as a bye-product in the preparation of the pyrazoline. 5-Methyl-3:5-dipropylpyrazoline boils at  $101$ — $103^{\circ}$  under 14 mm., at

113—115° under 20 mm. pressure; sp. gr. = 0.884 at 18°, 0.888 at 10°;  $n_D = 1.46318$ ; in other respects, it resembles the previous compound. 5-Methyl-3:5-dihexylpyrazoline is not formed very readily, and was obtained only in small amount.

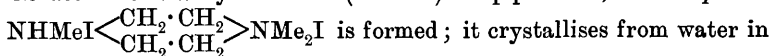
*Ethylideneazine*,  $\text{CHMe:N:N:CHMe}$ , can be prepared by shaking an ethereal solution of acetaldehyde with an aqueous solution of hydrazine hydrate, and cooling with water; it boils at 95—96° under 760 mm. pressure, and has sp. gr. = 0.832 at 17°; at 180°, it is almost unchanged, but at a higher temperature it gives off nearly all its nitrogen as gas, no butylene being formed, however; it is fairly stable towards alkalis, but acids decompose it into acetaldehyde and hydrazine. With maleic acid, it yields the *maleate* of 5-methylpyrazoline, and this, when decomposed with caustic potash, and the product fractionated, yields a small quantity of the pyrazoline, together with much of a bye-product (see below). The base boils at 73° under 55 mm., at 68° under 45 mm. pressure; the *benzoyl* derivative melts and decomposes at 156°; a red *tolueneazo*-derivative, with green reflex, was obtained; and with bromine in chloroform solution, 5-methylpyrazole appears to be formed. The bye-product mentioned above,  $\text{C}_{10}\text{H}_{20}\text{N}_6$ , possibly has the constitution



its *hydrochloride* and *picrate* melt and decompose at 148° and 142° respectively; it takes up 6Br, gives a yellow coloration with nitrous acid, colours wood yellow, and reduces ammoniacal silver solution.

C. F. B.

**Stereoisomerism in Piperazine and Ethylenediamine Derivatives.** By WILLEM VAN RIJN (*Chem. Centr.*, 1898, i, 727; from *Ned. Tijdsch. Pharm.*, 10, 43—52. See this vol., i, 77).—*Diethylpiperazine*, prepared by warming an aqueous solution of piperazine with an excess of potassium ethylic sulphate, is purified by crystallising the platinochloride from hot dilute hydrochloric acid. By the action of methylic iodide (4 mols.) on piperazine, the compound



small prisms, decomposes at 260° without melting, and, with cadmium iodide (1 mol.), forms a double salt which crystallises in small, white prisms. The compound  $\text{NEt} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{NEt}_2\text{I}$ , prepared by the action of ethylic iodide on piperazine, crystallises from alcohol in white needles, melts at 240°, and is insoluble in cold water, ether, chloroform, light petroleum, benzene, and carbon bisulphide; the cadmium iodide compound crystallises in white needles. The action of propylic iodide on piperazine is analogous to that of ethylic iodide. Attempts to prepare an isomeride of the hydrochloride of dibenzylpiperazine methiodide by the action of freshly precipitated silver chloride on the dibenzylpiperazine methiodide obtained from the hydrochloride by means of sodium hydroxide, resulted only in the production of the original compound. By the action of propylic iodide on methylethylethylenediamine, the mono- and di-propiodides



are formed, and may be separated by means of the platinochlorides. The platinochloride of the former crystallises in reddish needles, and that of the latter in reddish-yellow leaflets. No other salts could be obtained in a crystalline form.

E. W. W.

**Aromatic Diurethanes of Piperazine.** By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1897, 125, 1182—1184).—Molecular proportions of piperazine and phenylic carbonate, when heated in alcoholic solution for 20 hours, give an almost theoretical yield of the *diurethane*,  $\text{COOPh}\cdot\text{N}\cdot\text{C}_4\text{H}_8\cdot\text{N}\cdot\text{COOPh}$ , which forms prismatic crystals and melts at  $177\text{--}178^\circ$ ; its constitution is established by hydrolysis with potash, and by decomposition with concentrated sulphuric acid.

The  $\alpha$ - and  $\beta$ -*naphthyllic diurethanes*, prepared in a similar manner, form white, mammelated crystals somewhat insoluble in ordinary solvents; the  $\alpha$ -compound melts at  $190\text{--}191^\circ$ , the  $\beta$ - at  $220^\circ$ .

The *guaiacol derivative*,  $\text{C}_4\text{N}_2\text{H}_8(\text{COO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , crystallises from alcohol in plates and melts at  $181^\circ$ .

G. T. M.

**Derivatives of Triazole.** By JOHANNES THIELE and WILHELM MANCHOT (*Annalen*, 1898, 303, 33—56. Compare Thiele and Heidenreich, *Abstr.*, 1894, i, 57).—Formamidoguanidine *nitrate*,  $\text{COH}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2\cdot\text{HNO}_3$ , prepared by heating amidoguanidine nitrate with 90 per cent. formic acid and one drop of nitric acid on the water-bath, crystallises from water and melts at  $143^\circ$ ; the *picrate* crystallises in needles and melts at  $193^\circ$ . *Oxalylamidoguanidine*,  $\text{COOH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$ , obtained on adding amidoguanidine hydrogen carbonate to a concentrated aqueous solution of oxalic acid, and boiling the liquid in a reflux apparatus, crystallises from water, and melts and evolves gas at  $231\text{--}232^\circ$ .

Ammonia is readily eliminated from amidomethyltriazole under the influence of dilute sulphuric acid at  $180\text{--}190^\circ$ , the other products being carbonic anhydride, hydrazine, and acetic acid; a 30 per cent. solution of caustic potash or soda, however, leaves the amido-compound for the greater part unchanged. The *benzoyl* derivative of amidomethyltriazole melts and decomposes at  $285\text{--}290^\circ$ ; the *acetyl* derivative crystallises from water, and remains unfused at  $270^\circ$ .

*Methyltriazoleazodimethylaniline*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \text{N}\text{---}\text{CMe} \end{smallmatrix}$ , prepared by adding dimethylaniline hydrochloride to a solution of diazotised amidomethyltriazole, crystallises from alcohol, and melts and decomposes at  $238^\circ$ ; reduction with stannous chloride and hydrochloric acid destroys the colour, which is redeveloped under the influence of ferric chloride.

*Methyltriazoleazo- $\beta$ -naphthylamine*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \text{N}\text{---}\text{CMe} \end{smallmatrix}$ , is a red powder, with green, metallic reflex, and melts and decomposes at  $270^\circ$ . The colour is destroyed by reducing agents, and is not redeveloped by ferric chloride.

*Chloromethyltriazole*,  $\text{CCl}\begin{smallmatrix} \text{HN}\cdot\text{N} \\ \text{N}\text{---}\text{CMe} \end{smallmatrix}$ , obtained by diazotising amidomethyltriazole in concentrated hydrochloric acid, and evaporating the

liquid at the ordinary temperature, melts at  $147^{\circ}$ ; it is volatile in steam, and sublimes when heated on the water-bath. The *silver* derivative is sparingly soluble in water, but readily in ammonia and nitric acid.

*Benzylidenemethyltriazylhydrazine*,  $\text{CHPh}:\text{N}\cdot\text{NH}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagdown \quad \diagup \\ \text{N}-\text{CMe} \end{smallmatrix}$ , prepared by reducing diazotised amidomethyltriazole, under special precautions, and combining the product with benzaldehyde, crystallises from alcohol and melts at  $263^{\circ}$ ; the *hydrochloride* separates from alcohol in needles, and melts at  $256^{\circ}$ .

*Amidotriazole*,  $\text{NH}_2\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagdown \quad \diagup \\ \text{N}-\text{CH} \end{smallmatrix}$ , obtained on heating aqueous formamidoguanidine nitrate with sodium carbonate, crystallises from ethylic acetate and melts at  $159^{\circ}$ ; it closely resembles amidomethyltriazole, but differs from the latter, which is feebly alkaline and has no reducing action, whereas amidotriazole is neutral, and slightly reduces a boiling, ammoniacal solution of silver nitrate. The *nitrate* melts and decomposes at  $174^{\circ}$ , and the *picrate*, which crystallises in yellow needles, melts and decomposes at  $227-228^{\circ}$ . *Azotriazole*,  $\text{N}_2(\text{C}_2\text{H}_2\text{N}_3)_2$ , prepared by oxidising amidotriazole with potassium permanganate in alkaline solution, dissolves in alkalis, and is precipitated by acids. *Hydrazotriazole hydrochloride*, which is formed when azotriazole is reduced with stannous chloride and hydrochloric acid, crystallises in white needles and melts at  $227-230^{\circ}$ , beginning to decompose before this temperature is reached. It reduces ferric chloride and ammoniacal silver nitrate, and aqueous solutions readily undergo oxidation when exposed to the air. *Triazoleazodimethylaniline*, produced on adding dimethylaniline hydrochloride to a solution of diazotised amidotriazole, crystallises from alcohol, and melts and decomposes at  $250^{\circ}$ .

*Chlorotriazole*,  $\text{CCl}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagdown \quad \diagup \\ \text{N}-\text{CH} \end{smallmatrix}$ , prepared by diazotising amidotriazole in concentrated hydrochloric acid, crystallises from benzene in slender needles, and melts at  $167^{\circ}$ ; it sublimes when heated, and is volatile in vapour of benzene. It yields salts with acids, and also forms metallic derivatives.

*Amidotriazolecarboxylic acid*,  $\text{NH}_2\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \diagdown \quad \diagup \\ \text{N}-\text{C}\cdot\text{COOH} \end{smallmatrix}$ , obtained by heating oxalylamidoguanidine (2 mols.) with sodium carbonate on the water-bath, melts at  $182^{\circ}$  with elimination of carbonic anhydride and production of amidotriazole; it dissolves readily in alkalis, and is precipitated by acids. The *picrate* melts at  $176^{\circ}$ , and the *hydrochloride* melts and decomposes at  $171-172^{\circ}$ ; the *sodium* salt is anhydrous, and the *ethylic* salt crystallises from alcohol and melts at  $247^{\circ}$ .

*Diazotriazolecarboxylic acid*,  $\text{C}_3\text{HN}_5\text{O}_2 + \text{H}_2\text{O}$ , prepared by diazotising amidotriazolecarboxylic acid, decomposes at  $96^{\circ}$ ; it does not explode when touched with a hot wire, and detonates with difficulty when struck. Chlorotriazole is produced on heating the substance with hydrochloric acid, and triazole results from boiling an alcoholic solution in a reflux apparatus; triazole obtained in this manner melts

at 120—120·5°, and is identical with the compound described by Bladin and by Andreocci. M. O. F.

**Hydrazine Derivatives of Propionic Acid.** By JOHANNES THIELE and JAMES BAILEY (*Annalen*, 1898, 303, 75—91. Compare Thiele and Heuser, *Abstr.*, 1896, i, 340).—The *semicarbazone* of acetaldehyde crystallises from alcohol in white needles, and melts at 162°. *Carbonamidohydrazopropionitrile*,  $\text{NH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CN}$ , prepared by the action of 60 per cent. hydrocyanic acid on the semicarbazone of acetaldehyde, crystallises from alcohol and melts at 131°; it has a powerful reducing action, and yields hydrogen cyanide when heated. *Carbonamidohydrazopropionamide* is obtained by the action of cold concentrated hydrochloric acid on the nitrile for 24 hours; it separates from water in lustrous crystals containing  $\text{H}_2\text{O}$ , and melts at 99—106°, or at 142° in the anhydrous condition.

*Dihydroxymethyl-dihydrotriazine*,  $\text{OH}\cdot\text{C}\langle\begin{smallmatrix} \text{N}\cdot\text{C}(\text{OH}) \\ \text{NH}\text{---}\text{NH} \end{smallmatrix}\rangle\text{CMe}$ , prepared by treating the foregoing nitrile with fuming hydrochloric acid during 48 hours, diluting the liquid with twice its volume of water, and boiling the product for 3 hours in a reflux apparatus, crystallises from alcohol in lustrous scales and melts at 214°. *Dihydroxymethyl-triazine*,  $\text{OH}\cdot\text{C}\langle\begin{smallmatrix} \text{N}\cdot\text{C}(\text{OH}) \\ \text{N}=\text{N} \end{smallmatrix}\rangle\text{CMe}$ , is obtained by oxidising the dihydro-derivative with bromine water; it softens at 206° and melts at 209°.

The imido-ether of carbonamidohydrazopropionic acid is obtained in the form of the *hydrochloride*,



when an alcoholic solution of the nitrile is saturated with dried hydrogen chloride; it is very hygroscopic, deliquescent rapidly on exposure to the air, and melts at 124—128°, when it decomposes vigorously. On dissolving the hydrochloride in water, neutralising one-half of the hydrochloric acid with sodium carbonate, evaporating to dryness, and extracting with ethylic acetate, *ethylic carbonamidohydrazopropionate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOEt}$ , is produced; it melts at 108°. The free acid, obtained by hydrolysis with baryta, melts and decomposes at 166—168°. Hydrazidopropionic acid,  $\text{NH}_2\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOH}$ , prepared by the action of boiling 80 per cent. sulphuric acid on ethylic carbonamidohydrazopropionate, is identical with the compound described by W. Traube and Longinescu (*Abstr.*, 1896, i, 340).

The *semicarbazone* of pyruvonnitrile,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CN}$ , obtained by oxidising carbonamidohydrazopropionitrile with potassium permanganate, is a sparingly soluble crystalline powder, which melts and decomposes at 215°; the *semicarbazone* of pyruvamide and the semicarbazone of ethylic pyruvate melt and decompose at 230° and 206° respectively.

*Ethylic hydrazopropionate*,  $\text{N}_2\text{H}_2(\text{CHMe}\cdot\text{COOEt})_2$ , prepared, under specified conditions, from hydrazine, aldehyde-ammonia, and hydrogen cyanide, by hydrolysing an alcoholic solution of the product with hydrogen chloride, crystallises from benzene, petroleum, or water in thin, elongated prisms; it melts at 78°, and boils at 245°

under a pressure of 750 mm. The salt can also be obtained from hydrazidopropionic acid, aldehyde-ammonia, and hydrogen cyanide. The *methylic* salt melts at 93°, and boils at 220° under a pressure of 720 mm. The free *acid*, which crystallises from concentrated aqueous solutions in microscopic needles, begins to darken at 180°, and melts and evolves gas at 198°. M. O. F.

### Characteristic Oxidation Reaction of some Cyclic Amines.

By EUGEN BAMBERGER and ANTON VON GOLDBERGER (*Ber.*, 1898, 31, 2636—2640).—The authors have found that the hitherto unknown

izimidindazole,  $C_6H_4 \begin{smallmatrix} C(NH_2) \\ \diagup \quad \diagdown \\ N \end{smallmatrix} > NH$ , may be oxidised in various ways, but in most cases the product is Weddige and Fluger's hydroxy- $\beta$ -phenotriazine, the so-called benzazimide,  $C_6H_4 \begin{smallmatrix} C(OH) \cdot N \\ \diagup \quad \diagdown \\ N \end{smallmatrix}$

A similar change of structure occurs also when the monomethyl, and dimethyl-izimidindazoles are oxidised; these yield the corresponding monomethyl- and dimethyl-hydroxy- $\beta$ -phenotriazines.

Hydroxy- $\beta$ -phenotriazine partakes of the nature of a diazoamido-compound, as its formula indicates. It gives a brilliant red colour with  $\beta$ -naphthylamine, and with melted resorcinol it yields a colouring matter, *benzamidoazoresorcinol*, which crystallises in rosettes of dark-red needles. Its structure is probably  $NH_2 \cdot CO \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH)_2$ .

When izimidindazole is oxidised in alkaline solution by means of a ferricyanide or even by air, a basic *substance* is formed, which has colouring properties and forms crystals having an intense green metallic sheen; it gives a sparingly soluble nitrate, and may be diazotised. A. L.

**Azo- and Hydrazo-compounds of Tetrazole.** By JOHANNES THIELE (*Annalen*, 1898, 203, 57—75. Compare Abstr., 1894, i, 61). When amidotetrazole is oxidised by potassium permanganate in feebly alkaline solution, it is completely decomposed, but in presence of much alkali, derivatives of azotetrazole are produced. The *sodium*, *potassium*, and *barium* derivatives contain  $5H_2O$ , and the *calcium* derivative  $8H_2O$ , the *ammonium* derivative is anhydrous, and crystallises from water in yellow needles, which decrepitate at 210° without exploding. The *hydroxylamine* derivative contains  $2H_2O$ , and explodes violently at high temperatures; the *hydrazine* derivative also contains  $2H_2O$ , and the *amidoguanidine* derivative crystallises in long, yellow needles containing  $1H_2O$ . The *diazoguanidine* derivative,  $C_4H_8N_{20}$ , is anhydrous.

When an aqueous solution of azotetrazole is treated with excess of a mineral acid, tetrazylhydrazine is produced, with elimination of nitrogen and formic acid; oxalic acid gives rise to diazoimide. On adding dilute acid to an aqueous solution of sodium azotetrazole covered with ether, the latter takes up a considerable amount of azotetrazole; the yellow solution rapidly becomes turbid, however, from separation of a brick-red substance of unknown composition, but which probably contains one tetrazole ring.

Hydrazotetrazole, prepared by boiling an aqueous solution of sodium azotetrazole with magnesium powder, is a white, amorphous compound, insoluble in organic media, and dissolving with great difficulty in boiling water; the substance is precipitated by ammonia and alkalis from the solution in concentrated hydrochloric acid, and the aqueous solution yields precipitates with many metallic salts.

*Dibromoformaltetrazylhydrazone*,  $\text{CBr}_2 \cdot \text{N} \cdot \text{NH} \cdot \text{CN}_4\text{H}$ , obtained by the action of bromine water on a solution of hydrazotetrazole in concentrated hydrobromic acid, crystallises from ether in white needles containing  $\frac{1}{2}\text{H}_2\text{O}$ ; it becomes brown when heated, and melts at  $177^\circ$ . Concentrated sulphuric acid eliminates hydrogen bromide and carbonic anhydride, forming tetrazylhydrazine. Further treatment of hydrazotetrazole with bromine converts it into isocyanogen tetrabromide (*loc. cit.*).

*Methylic azinocarbonate*,  $\text{N}_2[\text{C}(\text{OMe})_2]_2$ , prepared by the action of potash dissolved in methylic alcohol on isocyanogen tetrabromide, separates from ethylic acetate in beautiful crystals, and melts at  $111^\circ$ ; dilute acids resolve the substance into methylic carbonate and hydrazine.

The *sodium* derivative of the amide of tetrazoleazocarboxylic acid, obtained by oxidising an alkaline solution of tetrazylsemicarbazide (Abstr., 1896, i, 107) with potassium permanganate, crystallises from water in lustrous, orange plates containing  $2\text{H}_2\text{O}$ ; caustic potash eliminates ammonia, and gives rise to the *potassium* salt of tetrazolecarboxylic acid, which is decomposed by dilute acids, yielding carbonic anhydride, formic acid, nitrogen, and hydrazine, not tetrazole. Tetrazoleazodimethylaniline is decomposed by dilute acids in the same way.

M. O. F.

**Derivatives of Amido-orceinol.** By FERDINAND HENRICH (*Monatsh.*, 1898, 19, 483—517. Compare Abstr., 1897, i, 446).—*Tribenzoylamido-orceinol*,  $\text{NHBz} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OBz})_3$ , formed when amido-orceinol is shaken with an excess of benzoic chloride and soda, crystallises from absolute alcohol in white, prismatic needles, melts at  $165$ — $166^\circ$  (uncorr.), dissolves readily in benzene, chloroform, and hot alcohol, fairly readily in cold alcohol, and sparingly in ether; it yields 3-hydroxy-2'-phenyl-1-methylbenzoxazole when distilled and hydrolysed.

3-Hydroxy-2'-phenyl-1-methylbenzoxazole has a normal molecular weight in boiling acetone, is not altered by boiling with strong hydrochloric acid, but is hydrolysed when heated with it, under pressure, at  $183^\circ$  for 5 hours, yielding benzoic acid and amido-orceinol.

3-Hydroxy-2'-phenylbenzoxazole, 
$$\begin{array}{c} \text{CH}:\text{CH}:\text{C}:\text{N} \\ | \quad | \quad | \\ \text{OH}:\text{C}:\text{CH}:\text{C}:\text{O} \end{array} \gg \text{CPh}$$
, is made by

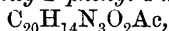
treating amidoresorcinol with benzoic chloride, heating the product for 15 minutes at its boiling point, and finally hydrolysing with alcoholic potash the benzoyl derivative thus obtained; it crystallises from benzene in colourless, compact crystals, melts at  $216$ — $217^\circ$ , dissolves readily in acetone, acetic acid, hot alcohol, and ether, but sparingly in light petroleum, cold chloroform, and benzene. Its alkaline solution is reddish-yellow and has a lilac fluorescence.

When 3-hydroxy-2'-phenyl-1-methylbenzoxazole is treated with strong nitric acid, the 2:4-dinitro-compound,  $\text{C}_{14}\text{H}_9\text{O}_2\text{N}(\text{NO}_2)_2$ , is formed. This separates from alcohol and chloroform in yellow, rhombohedral

crystals and melts at 188—189°, is sparingly soluble in cold alcohol, ether, acetic acid, and petroleum, but dissolves somewhat more readily in hot benzene and chloroform; it has very feeble tinctorial properties, decomposes carbonates, liberating carbonic anhydride, and gives a crystalline *sodium* salt.

3-Hydroxy-2'-phenyl-1-methylbenzoxazole is not affected by nitrous acid, but reacts in alkaline solution with diazobenzene, yielding *benzeneazo-3-hydroxy-2'-phenyl-1-methylbenzoxazole*,  $C_{20}H_{15}N_3O_2$ , which crystallises from glacial acetic acid in brownish-yellow needles and melts at 169—170°, dissolves readily in benzene and chloroform, but sparingly in cold alcohol and ether; sulphuric acid dissolves it, forming a yellowish-red solution which becomes redder on dilution. The *hydrochloride*,  $C_{20}H_{15}N_3O_2 \cdot HCl$  (?), separates on passing hydrogen chloride into an ethereal solution of the base; it decomposes very quickly in presence of moisture.

*Acetoxybenzeneazo-3-hydroxy-2'-phenyl-1-methylbenzoxazole*,



made by heating the foregoing base with acetic chloride and anhydrous sodium acetate, crystallises from alcohol in long, orange-coloured, apiculate prisms and melts at 182—183°; it is only slowly hydrolysed by boiling aqueous or alcoholic alkalis. The corresponding *hydrazo*-compound, made by heating it with zinc dust and acetic acid, crystallises from acetic acid in long leaflets and melts at 184—185°; it dissolves in strong sulphuric acid, giving a faintly coloured solution having a steel-blue fluorescence; on oxidation with nitrous acid, it yields the original hydroxyphenylmethylbenzoxazole. The corresponding *benzoyl* derivative,  $C_{20}H_{14}N_3O_2Bz$ , crystallises from absolute alcohol in light, brownish-yellow, prismatic, pointed crystals, sinters at 160°, and melts at 171°; it resembles the corresponding acetyl compound in its behaviour towards concentrated sulphuric acid and alkalis. On reduction, it yields a *compound* which dissolves in alkalis and in sulphuric acid, and the solution in the latter instance has a steel-blue fluorescence; it gives hydroxyphenylmethylbenzoxazole on treatment with nitrous acid.

*Paramethoxybenzeneazo-3-phenyl-1-methylbenzoxazole*,  $C_{20}H_{24}N_3O \cdot OMe$ , produced when the azo-compound is treated with sodium methoxide and methylic iodide, crystallises from absolute alcohol in small, yellow needles, sinters at about 135°, and melts at 149—150°; it dissolves readily in cold benzene, chloroform, ethylic acetate, ether, and hot alcohol, but only sparingly in light petroleum and cold alcohol.

3-Hydroxy-1 : 2'-dimethylbenzoxazole,  $\begin{array}{c} CH : CMe \cdot C : N \\ | \quad | \\ C(OH) : CH \cdot C \cdot O \end{array} \gg CMe$ , formed

when triacetyl-amido-orcinol is hydrolysed with diluted sulphuric acid or concentrated hydrochloric acid, crystallises from alcohol or benzene in long, colourless needles, melts at 210°, and dissolves readily in acetic acid, warm ether, and alcohol, but only sparingly in benzene and light petroleum. Its *acetyl* derivative,  $C_{11}H_{11}O_3N$ , formed by heating triacetyl-amido-orcinol at its boiling point for some time, crystallises from petroleum in white needles, melts at 65°, and is readily soluble in the ordinary media; it yields the preceding compound on hydrolysis with alcoholic potash. The *benzoyl* derivative,  $C_9H_8O_2N \cdot COPh$ ,

crystallises from petroleum, melts at 108—110°, and dissolves readily in the usual solvents, with the exception of light petroleum.

*Benzeneazo-3-hydroxy-1:2'-dimethylbenzoxazole*, made by the action of diazobenzene\* in alkaline solution on hydroxydimethylbenzoxazole, melts at 116—118°, and dissolves readily in the usual media; it behaves towards strong sulphuric acid like the corresponding derivative of phenylmethylbenzoxazole, but is much more readily soluble in soda.

*Formamido-orcinol*,  $C_7H_5(OH)_2 \cdot NH \cdot CHO$ , obtained when sodium formate and anhydrous formic acid are heated with amido-orcinol hydrochloride at the temperature of a glycerol bath, sinters at 180°, melts and becomes red at 195—198°, and dissolves readily in alcohol and hot water, somewhat sparingly in ether, benzene, and chloroform, and is insoluble in light petroleum. It is quickly dissolved by aqueous soda, and reduces Fehling's solution and ammoniacal silver nitrate.

*3-Hydroxy-1-methylbenzoxazole*,  $OH \cdot C_7H_5 \cdot \begin{smallmatrix} N \\ \diagup \diagdown \\ O \end{smallmatrix} CH$ , produced when the formyl compound is heated at 208°, forms long, colourless leaflets and melts at 162—163° after sintering slightly; it is readily soluble in acetic acid, alcohol, and ether, somewhat readily in benzene, and sparingly in chloroform and light petroleum, especially in the cold; it dissolves in strong soda ley, forming a colourless solution, but is not dissolved by a dilute solution of soda; it yields amido-orcinol when hydrolysed by strong hydrochloric acid.

*3-Benzoxoy-1-methylbenzoxazole*,  $C_8H_6NO_2Bz$ , is readily soluble in alcohol, ether, benzene, acetic acid, carbon bisulphide, and chloroform, but only sparingly in cold petroleum. It is insoluble in alkalis, melting to an oil when warmed with them. *Benzeneazo-3-hydroxy-1-methylbenzoxazole*,  $C_{14}H_{11}N_3O_2$ , forms elongated leaflets having an intense purple colour, and melts at 186°; it dissolves readily in benzene and chloroform, but only sparingly in petroleum and in cold alcohol or acetone; it forms a yellowish solution in strong sulphuric acid, which becomes a deeper red on dilution, and dissolves more readily in aqueous soda than do the corresponding 2'-phenyl- and 2'-methyl-derivatives.

A. L.

**New Synthesis of Paraxanthine.**—By EMIL FISCHER and HANS CLEMM (*Ber.*, 1898, 31, 2622—2623).—*Chloroparaxanthine*,  $NMe \cdot CO \cdot C \cdot NMe$   
 $CO \cdot NH \cdot C \text{---} N \geq CCl$ , is formed when 1:7-dimethyluric acid is heated with phosphorus oxychloride at 135—140° for 3 hours, and can be purified by boiling with alcohol and subsequent recrystallisation from a large bulk of hot water; it melts at 284° (295° corr.), dissolves in 170 parts of hot water, and crystallises from it on cooling in colourless, interlacing prisms; it is more readily soluble in hot alcohol. When heated, it melts and sublimes readily, slight decomposition occurring. The *sodium* salt is sparingly soluble in cold water, and separates from hot water in slender, shining needles; the *potassium* salt is more readily soluble, and crystallises in spherical aggregates of slender, colourless needles. Chloroparaxanthine dissolves readily in cold dilute ammonia, and the solution gives, with silver nitrate, a white, amorphous precipitate which blackens when

warmed, and dissolves in warm dilute nitric acid, the solution depositing slender needles on cooling.

Chloroparaxanthine is readily reduced to paraxanthine when warmed with hydriodic acid and phosphonium iodide. A. L.

**Xanthine Bases from Uric Acid.** By ERNST E. SUNDBVIK (*Zeit. physiol. Chem.*, 1898, 26, 131—132).—In a previous paper (Abstr., 1897, i, 598), it is stated that, by reduction of uric acid, xanthine and hypoxanthine are probably formed. This view is now shown to be correct, the bases having been isolated and analysed. W. D. H.

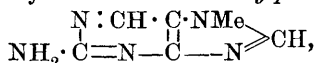
**Some Properties of Caffeine.** By E. TASSILLY (*Bull. Soc. Chim.*, 1897, [iii], 17, 596—599).—Hydrated caffeine,  $C_8H_{10}N_4O_2 + H_2O$ , does not lose all its water of crystallisation even at  $150^\circ$ , at which temperature it is partially volatile. At  $110^\circ$ , the anhydrous compound does not lose in weight, whereas the hydrate undergoes a loss of 6.93 per cent. Caffeine is not volatile with steam. Calcium hydroxide solution decomposes the alkaloid at  $100^\circ$ , ammonia being evolved, whilst with magnesia under similar circumstances no trace of ammonia is given off. The partition of caffeine between different solvents ceases to be normal when other extractive substances are present. J. J. S.

**Hydurinephosphoric Acid.** By EMIL FISCHER (*Ber.*, 1898, 31, 2547—2549).—Finely-powdered trichloropurine,  $C_5H_3N_4Cl_3$ , is added to 10 times its weight of hydriodic acid (sp. gr. 1.96), excess of powdered phosphonium iodide added, and the mixture kept, first for an hour at  $0^\circ$  with frequent shaking, and then shaken at the ordinary temperature for 24 hours by means of a motor; the product is then warmed to  $40^\circ$ , filtered, evaporated at  $40$ — $50^\circ$  under diminished pressure, mixed with a little water, and again evaporated; the crystalline residue is washed with a little cold water and recrystallised from dilute hydriodic acid, warming gently only. In this way, the *hydriodide* of hydurinephosphoric acid,  $C_4H_9N_4PO_3 \cdot HI + H_2O$ , is obtained; by treatment with water and freshly precipitated silver iodide, it can be converted into the *hydrochloride*,  $C_4H_9N_4PO_3 \cdot HCl$ . These salts are soluble in water, but the solution soon turns red; this coloration is hindered by the presence of a little halogen acid, but promoted by alkalis, the colour when ammonia is present becoming eventually that of a potassium permanganate solution. When heated with dilute hydrochloric acid on the water-bath, the hydrochloride yields ammonium chloride and phosphoric acid, but no phosphorous acid. The base corresponding with these salts is *hydurinephosphoric acid*, which is probably  $C_4H_7N_4 \cdot PO(OH)_2$ , derived from a hypothetical base hydurine,  $C_4H_8N_4$ , in the same way as is the amidophosphoric acid,  $NH_2 \cdot PO(OH)_2$ , from ammonia,  $NH_3$ . C. F. B.

**Purine and its Methyl Derivatives.** By EMIL FISCHER (*Ber.*, 1898, 31, 2550—2574).—*2-Iodo-7-methylpurine*, 
$$\begin{array}{c} N:CH \cdot C \cdot NMe \\ | \\ Cl:N \cdot C \text{---} N \text{---} CH \end{array}$$
 is obtained by reducing 2:6-dichloro-7-methylpurine (Abstr., 1898, i, 97) with hydriodic acid in large excess and phosphonium iodide at  $0^\circ$ ;



it melts at  $229^{\circ}$  (corr.). When boiled with normal potash, it is converted into 2-oxy-7-methylpurine,  $\begin{array}{c} \text{N}:\text{CH}-\text{C}\cdot\text{NMe} \\ | \quad | \\ \text{C}\cdot\text{O}\cdot\text{NH}\cdot\text{C}-\text{N} \end{array} \gg \text{CH} + \text{H}_2\text{O}$ , which decomposes at about  $323^{\circ}$ , and with normal potassium hydrosulphide solution in large excess, into an analogous, yellow *thio*-compound which decomposes at about  $295^{\circ}$ . With half-saturated alcoholic ammonia at  $145-150^{\circ}$ , it yields 2-amido-7-methylpurine,



melting at  $283^{\circ}$  (corr.), which can also be obtained from 2-chloro-7-methylpurine (see below), a compound that is more easily prepared than 2-iodo-7-methylpurine. When boiled with zinc dust and water,

it yields 7-methylpurine,  $\begin{array}{c} \text{N}:\text{CH}\cdot\text{C}\cdot\text{NMe} \\ | \quad | \\ \text{CH}\cdot\text{N}\cdot\text{C}-\text{N} \end{array} \gg \text{CH}$ ; this melts at  $184^{\circ}$  (corr.), its *mercurichloride* at  $252^{\circ}$  (corr.), and its *methiodide* at  $231-232^{\circ}$  (corr.).

2-Chloro-7-methylpurine,  $\begin{array}{c} \text{N}:\text{CH}\cdot\text{C}\cdot\text{NMe} \\ | \quad | \\ \text{CCl}\cdot\text{N}\cdot\text{C}-\text{N} \end{array} \gg \text{CH}$ , obtained by boiling 2:6-dichloro-7-methylpurine or trichloro-7-methylpurine with zinc dust and water, melts at  $200-201^{\circ}$  (corr.), the *mercurichloride* at  $206-207^{\circ}$ . When it is boiled with normal potash solution, a compound,  $\text{C}_5\text{H}_7\text{N}_4\text{Cl}$ , which melts and decomposes at about  $251^{\circ}$ , is deposited, whilst 2-oxy-7-methylpurine remains dissolved in the alkali.

2:6-Di-iodopurine,  $\begin{array}{c} \text{N}:\text{Cl}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{Cl}\cdot\text{N}\cdot\text{C}-\text{N} \end{array} \gg \text{CH}$ , obtained by heating trichloropurine (Abstr., 1898, i, 47) with hydriodic acid and phosphonium iodide, melts and decomposes at about  $224^{\circ}$ ; when heated with hydrochloric acid (sp. gr. = 1.19) at  $100^{\circ}$  in a sealed tube, it yields xanthine, and when boiled with zinc dust and water, the insoluble zinc salt of purine itself is formed, and remains mixed with the excess of zinc dust. Purine,  $\begin{array}{c} \text{N}:\text{CH}\cdot\text{C}\cdot\text{NH} \\ | \quad | \\ \text{CH}\cdot\text{N}\cdot\text{C}-\text{N} \end{array} \gg \text{CH}$ , is a readily soluble, well crystallised substance, which forms salts both with acids and with bases, and as regards its character in general falls naturally in the series uric acid, xanthine, hypoxanthine, purine. It melts at  $216-217^{\circ}$  (corr.); the *nitrate*, with  $1\text{HNO}_3$ , melts and decomposes at about  $205^{\circ}$ ; the yellow *picrate*, with  $1\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , melts at about  $208^{\circ}$ ; the base is very stable towards oxidising agents, and in consequence does not give the murexide reaction.

2(?)-Chloro-9-methylpurine, prepared by boiling trichloro-9-methylpurine (see below) with zinc dust and water, melts at  $135-136^{\circ}$  (corr.). When heated with half-saturated alcoholic ammonia at  $150^{\circ}$ , it is converted into 2(?)-amino-9-methylpurine, which melts at  $247^{\circ}$  (corr.); with hydriodic acid (sp. gr. = 1.96) at the ordinary temperature, it yields 2(?)-iodo-9-methylpurine melting at  $171-172^{\circ}$  (corr.). This, when boiled with zinc dust and water, yields 9-methylpurine,  $\begin{array}{c} \text{N}:\text{CH}\cdot\text{C}-\text{N} \\ | \quad | \\ \text{CH}\cdot\text{N}\cdot\text{C}\cdot\text{NMe} \end{array} \gg \text{CH}$ , which melts at  $162-163^{\circ}$  (corr.).

*Preparation of Trichloro-9-methylpurine.*—This is best prepared with-

out the use of phosphoric chloride; 2:6-dichloro-8-oxy-9-methylpurine (1 part) is heated with phosphorus oxychloride (25 parts) for 10 hours at 160—165°, the product is evaporated under diminished pressure, and the residue washed with cold water and then with cold dilute caustic soda, and recrystallised from alcohol.

*Identification of Xanthine.*—This is best effected by heating the supposed xanthine (1 part) with bromine (5 parts) at 100° in a sealed tube, opening the tube and heating it to 140—145° to expel bromine, washing the residue with sulphurous acid, dissolving it in warm ammonia and precipitating with hot, dilute sulphuric acid. The bromoxanthine formed (1 part) is dissolved in normal caustic potash (13 parts by vol.), and heated with methylic iodide (2½ parts) in a sealed tube at 80° with constant shaking for 2 hours; the bromocaffeine which separates is washed with very dilute caustic soda and recrystallised from water; it melts at 206°. This (1 part) is boiled for 5 minutes with 10 per cent. alcoholic potash (7 parts), the mixture is diluted with 3 times its volume of water, and the ethoxycaffeine, which soon separates, is recrystallised from water; it melts at 140°. By boiling it (1 part) with 10 per cent. hydrochloric acid (10 parts by vol.) it can be converted into hydroxycaffeine, which melts at 345°. All these processes can be carried out with 0.5 gram of xanthine, and in the space of 24 hours. C. F. B.

**Behaviour of 2-Amido-6:8-dioxypurine towards Chlorides of Phosphorus.** By EMIL FISCHER (*Ber.*, 1898, 31, 2619—2621).—

6-Chloro-2-amido-8-oxy<sup>6</sup>purine,  $\text{NH}_2 \cdot \text{C} \begin{array}{c} \text{N}:\text{CCl} \cdot \text{C} \cdot \text{NH} \\ \text{---} \text{N} \cdot \text{C} \cdot \text{NH} \end{array} > \text{CO}$ , made by boiling 2-amido-6:8-dioxypurine with phosphorus pentachloride dissolved in phosphorus oxychloride, can be purified by dissolving it in warm dilute ammonia and treating with animal charcoal; the filtered liquid, heated to drive off ammonia, deposits the substance in bundles of slender, microscopic needles. It decomposes at a high temperature without melting, dissolves sparingly in hot water and still more sparingly in alcohol, is readily soluble in warm dilute mineral acids, and fairly readily in dilute ammonia. When heated at 130° with hydrochloric acid, it yields the hydrochloride of 2-amido-dioxypurine.

When 6-iodo-2-amido-8-oxy<sup>6</sup>purine,  $\text{C}_5\text{H}_4\text{N}_5\text{OI}$ , obtained when chlor-amido-oxy<sup>6</sup>purine is heated with fuming hydriodic acid and phosphonium iodide at 100°, it is converted into a colourless, granular, indistinctly crystalline powder, which resembles in properties the original chloro-compound, but is more sparingly soluble. A. L.

**Bases Isomeric with Cinchonine.** By VICTOR CORDIER VON LOWENHAUPT (*Monatsh.*, 1898, 19, 461—482).—When cinchonine hydrobromide is heated with alcoholic potash, a mixture of bases is obtained which may be separated, by means of ether, into two portions. The least soluble portion may be further resolved by crystallisation from alcohol, and on treatment with sulphuric acid gives a salt,  $(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O})_2 \cdot \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , which has the same crystalline form as Hesse's homocinchonine sulphate (*Abstr.*, 1881, 615) and melts at 199.5°, and also the sulphate of a new base, *tautocinchonine*. This

base resembles homocinchonine in some respects; it dissolves in 144 parts of absolute alcohol at  $20^{\circ}$ , melts at  $252.5^{\circ}$ , and has  $[\alpha]_D = +209.42^{\circ}$ ; its *dihydriodide*,  $C_{19}H_{22}N_2O \cdot 2HI$ , forms beautiful, yellow prisms and melts at  $238^{\circ}$ .

If that portion of the product of hydrolysis of cinchonine hydrobromide which is readily soluble in ether is treated with hydrochloric acid and potassium iodide, it yields  *$\alpha$ -isocinchonine dihydriodide*, which forms beautiful, yellow, prismatic crystals, and melts at  $205-206^{\circ}$ , whilst the mother liquor from which it has been deposited contains a mixture of bases, and by successive treatment with hydrochloric acid and zinc chloride may be made to yield  $\delta$ -cinchonine hydrochloride and the zincchloride of a new base,  *$\epsilon$ -cinchonine*.

When cinchonine hydrobromide is hydrolysed with alcoholic silver nitrate, a mixture of bases is obtained which appear to be identical with those produced when alcoholic potash is employed, and only differ in their relative proportions.

*$\epsilon$ -Cinchonine*,  $C_{19}H_{22}N_2O$ , melts at  $152^{\circ}$ , dissolves very readily in alcohol, but more sparingly in ether; it crystallises from the latter in long, slender needles, and its specific rotation in 1 per cent. alcoholic solution at  $20^{\circ}$   $[\alpha]_D = 66.99$ . Its *hydrochloride*,  $C_{19}H_{22}N_2O \cdot HCl$ , is anhydrous and crystallises in thick prisms.

When water is used to hydrolyse cinchonine hydrobromide, a product is obtained from which ether dissolves  $\delta$ -cinchonine and  $\alpha$ -isocinchonine, leaving pseudocinchonine and what is probably apoisocinchonine (allocinchonine?).

When hydrobromic acid acts on cinchonine, not only is cinchonine hydrobromide formed, but the hydrobromides of  $\alpha$ -isocinchonine, pseudocinchonine, and  $\delta$ -cinchonine are also produced. A. L.

**Cinchonicine.** By FERDINAND ROQUES (*Ann. Chim. Phys.*, 1897, [vii], 10, 234—288).—The production of crystallised cinchonicine has already been described (*Abstr.*, 1895, i, 688). Full details of the method employed are set forth in the paper; the specific rotation of the base obtained either from cinchonine or cinchonidine is now given as  $[\alpha]_D = 57.60^{\circ}$ ; it was formerly stated to be  $48.25^{\circ}$ . The base from either of the two alkaloids melts at  $49-50^{\circ}$ , differing in this respect from von Miller and Rhode's cinchotoxine, which melts at  $58-59^{\circ}$ ; the two bases are otherwise very similar, and they may be identical (compare *Abstr.*, 1895, i, 434).

The *basic nitrate* crystallises readily in prisms, which melt and decompose at  $160^{\circ}$ ;  $[\alpha]_D = 29.58^{\circ}$ , the *normal nitrate* in yellow, silky needles, extremely soluble in water; its alcoholic solution is yellow, the colour disappearing when half the acid is neutralised by potash. The *normal succinate*,  $C_{19}H_{22}N_2O \cdot C_4H_6O_4 + H_2O$ , crystallises in prisms.

The double zinc and cadmium chlorides, and the alkylic haloid salts have already been described (*Abstr.*, 1895, i, 688). G. T. M.

**Chemistry of the Atropine Alkaloids.** By ADOLF PINNER (*Chem. Centr.*, 1898, i, 679; from *Centr. prakt. Augenheilk.*, 20, 1—9).—According to the author, the plants of the order of *Solanaceæ*, and the

species *Atropa*, *Hyoscyamus*, *Datura*, *Mandragora*, *Solanum*, and *Anisodus* contain at least the two alkaloids, hyoscyamine,  $C_{17}H_{23}NO_3$ , and hyoscyne (scopolamine). The former, by the action of alkalis, yields atropine, which may, perhaps, occur in small quantities in the plants, whilst hyoscyne, with alkalis, forms inactive scopolamine (atroschine). By the loss of water, hyoscyamine and atropine form apoatropine, which, by an intramolecular change, yields belladonnine. Atropine is always present in commercial hyoscyamine and inactive hyoscyne (atroschine), hyoscyamine and atropine are contained in commercial scopolamine, whilst duboisine contains hyoscyamine, hyoscyne, and other alkaloids. All the alkaloids, when hydrolysed, yield tropic acid;  $C_9H_{10}O_3$ , and tropine,  $C_8H_{15}NO$ , is formed from atropine, and oscine (scopoline),  $C_8H_{13}NO_2$ , from hyoscyne-scopolamine; the alkaloids can be partially regained from these products. E. W. W.

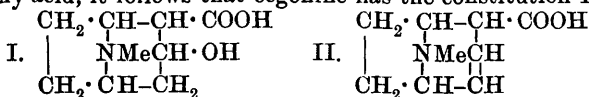
**Ketones of the Tropine Group. XII. Constitution of Ecgonine.** By RICHARD WILLSTÄTTER and WILHELM MÜLLER (*Ber.*, 1898, 31, 2655—2669. Compare *Abstr.*, 1898, i, 603).—*Hydroecgonidineamide*,  $C_8H_{14}N \cdot CO \cdot NH_2$ , prepared by the action of ammonia on the ethylic salt of hydroecgonidine, crystallises in long, six-sided tablets melting at 126—127°. When this substance is heated with

$$\begin{array}{c} CH_2 \cdot CH \cdot CH \cdot NH_2 \\ | \quad | \quad | \\ CH_2 \cdot CH \cdot CH \cdot NMeCH_2 \\ | \quad | \quad | \\ CH_2 \cdot CH \cdot CH_2 \end{array}$$

potassium hypobromite, it yields *isotropylamine*,

which is isomeric with the tropanylamines formed by the reduction of tropinonoxime; it is a colourless oil, which boils at 206—207° (corr.), and solidifies at 8.5°. The *mercurichloride* is soluble in hot water, and crystallises in characteristic tablets; the *hydrochloride* crystallises in compact, six-sided tablets, and sublimes when carefully heated; the *picrate* melts and decomposes at 236—237°, and the *platinochloride* decomposes at 261°, whilst the aurichloride could not be obtained of definite composition. The *thiocarbamide*,  $NHPh \cdot CS \cdot NH \cdot C_8H_{14}N$ , crystallises in colourless, swallow-tail forms, and melts at 138—139°. Nitrous acid does not convert the base into isotropine, but into tropidine. Isotropylamine can also be prepared from hydroecgonineamide by Curtius' method. The *hydrazide* forms a *picrate* melting at 172°, and, when treated with nitrous acid, yields *di-isotropylcarbamide*, from which isotropylamine can be prepared by the action of hydrochloric acid.

When ecgonine is oxidised by means of chromic acid, it yields tropinone, and this reaction shows that the hydroxyl group of ecgonine is in the same position as that of tropine and  $\psi$ -tropine. Moreover, since the properties of ecgonine are those of a  $\beta$ - and not of a  $\gamma$ -hydroxy-acid, it follows that ecgonine has the constitution I.



Anhydroecgonine, therefore, has the constitution II, which is in harmony with the formation from it of  $\delta$ -cycloheptatrienecarboxylic acid melting at 32°; this, as shown by its behaviour to alcoholic

potash (Einhorn and Willstätter, *Abstr.*, 1895, i, 92), does not contain an ethylene linking in the  $\Delta^1$ -position. A. H.

**Alkaloidal Constituents of Cascarilla Bark.** By WILLIAM A. H. NAYLOR (*Pharm. J.*, 1898, 59, 279).—Two bases are obtained by extracting the powdered bark with chloroform water containing 3 per cent. of oxalic acid. The one allied to choline forms a platinochloride crystallising in yellow, hexagonal plates, and a crystalline hydrochloride which gives off trimethylamine on heating; analysis of the former salt indicates that the base is in reality, not choline, but betaine. The second base, *cascarilline*, isolated for the first time, forms a buff-coloured *platinochloride*, which is soluble in alcohol and crystallises from water in prismatic plates. G. T. M.

**Antipeptone.** By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1898, 26, 110—122. Compare *Abstr.*, 1898, i, 611).—Antipeptone is not a peptone, neither is it a chemical unit (carnic acid) as alleged by Siegfried. It is a mixture of heterogeneous substances which, by means of phosphotungstic acid, can be divided into two parts, basic and acid. Among the bases, histidine, arginine, and another base of unknown nature were found; among the acids, aspartic acid was separated. W. D. H.

**Guanylic Acid from Pancreas and its Decomposition Products.** By IVAR BANG (*Zeit. physiol. Chem.*, 1898, 26, 133—159).—The *potassium* salt of guanylic acid, obtained by heating pancreas or nucleoproteid on the water-bath with 2 per cent. caustic potash, separates from the filtered extract as a voluminous sediment, which redissolves in hot water without decomposition, and is again precipitated as the solution cools. After repeating this treatment several times, the salt gives neither the Millon nor the biuret reaction. The free *guanylic acid* liberated by the addition of 5 per cent. acetic acid to the warm solution of the potassium salt, is obtained, after washing with alcohol and ether, in the form of a white powder. The other nucleic acids are not liberated from their salts by acetic acid, but in this case the free acid is obtained, and the use of acetic acid is preferable, since guanylic acid is slowly decomposed by hydrochloric acid at ordinary temperatures. Guanylic acid may be prepared directly from nucleoproteid by extraction with hot water, but the yield is smaller than by the above process. The free acid has a feebly acid reaction; it dissolves readily in alkalis and ammonia, and also in dilute mineral acids; its aqueous solution gives precipitates with solutions of the heavy metals, but not with albumin dissolved in dilute acetic acid, an acidic solution forms precipitates with phosphotungstic, tannic, and picric acids. Neither iron nor sulphur are present in guanylic acid; it contains less phosphorus and more nitrogen than the other nucleic acids, the ratio of these elements being P : 3N, whereas in the latter compounds it is P : 5N; hence the latter ratio can no longer be regarded as characteristic of these compounds. The analytical results agree most closely with the formula  $C_{22}H_{34}N_{10}P_2O_{17}$ , and although it is unlike other nucleic acids in composition and in many of its properties, the products of its decomposition show it to be closely related

to this class of substances. On boiling guanylic acid with dilute mineral acids, it decomposes, yielding a substance belonging to the pentose group, guanine, phosphoric acid, and ammonia. The exact nature of the pentose derivative has not been determined; it reduces Fehling's solution, forms an osazone melting at 151—154°, is unfermentable, and cannot be obtained crystalline; the quantity produced, calculated in terms of glucose, amounts to about 30 per cent. of the original substance. Nine-tenths of the nitrogen originally present in guanylic acid is obtained, after hydrolysis, in the form of guanine; this is the first example of a nucleic acid giving rise to only one xanthine base, and it is on this account that the name guanylic acid is given to the compound.

The only other nitrogenous product of decomposition is ammonia; no trace of thymine could be obtained, either from guanylic acid or from nucleoproteid. G. T. M.

**Ovimucoid and a New Glucoproteid from Blood-serum.** By CARLO U. ZANETTI (*Chem. Centr.*, 1898, i, 624—625; from *Ann. Chim. Farm.*, 26, 529—534. Compare Henriques, *Abstr.*, 1897, 570).—The author attributes the reducing action of blood to the presence of a substance which is closely related to, or identical with, ovimucoid. Ovimucoid is prepared from egg-albumin by dissolving it in 10 times its volume of a 5 per cent. solution of sodium chloride, adding acetic acid, removing the albumin and globulin by coagulating, filtering, concentrating, and finally precipitating with alcohol. It can be purified by dissolving in water and precipitating with alcohol, the sodium chloride being removed by dialysing. The white, pulverulent mass contains C = 48.75—48.94, H = 6.9—6.94, N = 12.46, S = 2.22 per cent., and with hydrochloric acid gives glucosamine, and one third of its sulphur in the form of sulphuric acid. The serum of the blood of oxen yields a similar substance, possibly identical with ovimucoid.

E. W. W.

**Existence of the Proteid Radicle suggested by Bertrand in the Oxydases.** By JOSEPH DE REY-PAILHADE (*Bull. Soc. Chim.*, 1897, [iii], 17, 756—757).—It has been suggested by Bertrand (*Abstr.*, 1897, ii, 493) that the oxydases contain a radicle of proteid character capable of entering into loose combination with manganese or hydrogen, and the author points out that philothion, a substance discovered by him in 1889 and subsequently described on many occasions, possesses the properties required of such a compound. The existence of philothion and analogous substances in animal tissues in the presence of manganese suggests a series of combinations and decompositions which offer a clear explanation of the mechanism of respiration in the tissues. N. L.

## Organic Chemistry.

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**Reductions in the Presence of Palladium.** By NICOLAI D. ZELINSKY (*Ber.*, 1898, 31, 3203—3205).—Experiments have previously been made with palladium-hydrogen as a reducing agent by Graham (*Annalen Sup.*, 1867, 5, 1) and by Saytzeff (*J. prakt. Chem.*, 1872, [ii], 6, 128); the author finds that it may be employed with great success in the reduction of iodides and bromides of cyclic alcohols, compounds which it has hitherto been impossible to reduce by any of the ordinary methods. Zinc filings are well washed with alcohol, then with dilute sulphuric acid until a vigorous evolution of gas begins, and finally with water; a 1—2 per cent. palladium chloride solution, which has been acidified with hydrochloric acid, is poured in and almost immediately a thin, adhesive layer of palladium is deposited on the zinc. This palladium-zinc couple, when washed with alcohol and, when necessary, dried, is ready for use. The reduction, as a rule, takes place readily at the ordinary temperature, but a temperature of 100° may also be employed. A flask filled to one-third with the zinc-palladium is provided with a reflux condenser and dropping funnel, the couple is partly covered with methylic or ethylic alcohol and hydrochloric acid saturated at 0° run in drop by drop, at first the hydrogen is absorbed by the palladium, but as soon as bubbles of the gas are evolved the bromide or iodide to be reduced may be added in small quantities, and then more hydrochloric acid, the quantities being so regulated that the reaction does not become too violent. In case any volatile hydrocarbon may be carried over, the gases evolved are bubbled through a wash bottle containing alcohol. The zinc-palladium remaining in the flask may be washed with hydrochloric acid and with alcohol, and is then ready for further use. J. J. S.

**Decomposition of a Normal Saturated Hydrocarbon by Aluminium Chloride.** By CHARLES FRIEDEL and ALEXANDRE GORGEU (*Compt. rend.*, 1898, 127, 590—594).—In extension of the work of Friedel and Crafts on the decomposition of aromatic hydrocarbons by aluminium chloride, the authors have investigated its action on pure normal hexane. This was heated on the water-bath, in successive small quantities, with well-powdered, freshly prepared aluminium chloride; on passing the products of the action, after removing the hydrogen chloride formed, through a U-tube cooled by a freezing mixture, a mobile liquid condensed which consisted principally of pentane, boiling at 35°. The gases formed in the action were collected over mercury, and found to consist principally of normal butane, identified by its boiling point and solubility in amyl alcohol; a small quantity of propane was, however, also present. The action thus consisted essentially in the substitution of successive methyl groups, at the end of the chain, by hydrogen atoms. In addition to the hydrocarbons isolated, richer in hydrogen than hexane, products richer in carbon were probably formed; on treating the aluminium chloride

used with water, and shaking with ether, a brownish, viscous liquid was obtained, which was, however, not further investigated.

The solubility in amylic alcohol of the paraffins gaseous at ordinary temperatures was determined as a means of recognising their presence in the gaseous product obtained in the above work; in using amylic alcohol for dissolving gases, care must be taken that the air, which it dissolves to the extent of 10 per cent., has been previously expelled by boiling. The methane and ethane employed were prepared by decomposing mercury-methyl and mercury-ethyl at 70—80° by dilute sulphuric acid from which air had previously been expelled; the propane and butane were obtained respectively from isopropyl and secondary butyl iodide by the action of zinc in presence of a very small quantity of hydrochloric acid, and were freed from hydrogen by being dissolved in amylic alcohol and subsequently liberated by heating. The solubilities are as follows: 1 vol. of amylic alcohol boiling at 130—132° dissolves, at 12·5°, 0·05 vol. of hydrogen under a pressure of 750 mm., and 0·5 vol. of methane under normal pressure; whilst 3·3 vols. of ethane are dissolved at 14°, and 12 vols. of propane at 16° under a pressure of 750 mm. Under a pressure of 760 mm., 11 vols. of propane are dissolved at 23°, and 44 vols. of butane at 22°, whilst 72 vols. of the latter gas are dissolved at 13° under a pressure of 740 mm.

W. A. D.

**Synthesis of Ethylic Alcohol.** By FRANK WOOD (*Chem. News*, 1898, 78, 308).—Alcohol was not obtained under the following circumstances. When acetylene, from calcium carbide, and hydrogen were passed through a calcium chloride tube, then through 18 inches of red hot combustion tube containing asbestos wool, and finally into pure sulphuric acid either cold or heated to 170°, the acid being then diluted largely and distilled; or when the gases from the action of dilute sulphuric acid on a mixture of calcium carbide and zinc dust, or of copper acetylide and zinc dust were treated in a similar manner, or when the gas evolved from the action of ammonia on the mixture of copper acetylide and zinc dust was passed into strong sulphuric acid, &c.

D. A. L.

**Normal Cyanobutylic Alcohols.** By LOUIS HENRY (*Chem. Centr.*, 1898, i, 984—985; from *Bull. Acad. roy. Belg.*, [iii], 35, 173—181).—*α-Hydroxybutyronitrile* (*α-cyanopropyl alcohol*), prepared from hydrocyanic acid and propaldehyde, is a rather viscous, colourless liquid with a bitter-sweet taste, has a sp. gr. = 1·0238 at 11°, and is insoluble in carbon bisulphide but soluble in water, alcohol, ether, chloroform, benzene, and acetone. It easily unites with amido- and imido-bases with loss of water, and when heated, decomposes into hydrogen cyanide and propaldehyde. The *acetyl* derivative,  $\text{CN} \cdot \text{CH}(\text{OAc}) \cdot \text{CH}_2\text{Me}$ , prepared by the action of acetic anhydride and acetic chloride on the nitrile, boils at 185—186°. *β-Hydroxybutyronitrile* (*β-cyanoisopropyl alcohol*) is obtained by the action of potassium cyanide on propylene monobromhydrin or iodhydrin; it is a rather viscous, colourless liquid with a faint odour and sweetish taste, boils at 220—221° under 757 mm., and at 123—125° under 22 mm. pres-



sure, is soluble in water, alcohol, and ether, insoluble in carbon bisulphide, and does not react with amido- or imido-bases. The *acetate* boils at  $210^{\circ}$  under 765 mm. pressure. The *ethoxy*-derivative boils at  $173-174^{\circ}$ .  $\gamma$ -Hydroxybutyronitrile ( $\gamma$ -cyanopropyl alcohol) can be prepared by the action of potassium cyanide on trimethylene iodhydrin, or from  $\gamma$ -chlorobutyric acid by hydrolysing the acetate by means of powdered sodium or potassium hydroxide, and distilling under diminished pressure; it is a rather viscous, colourless oil with a sharp, pungent taste and faint odour, is soluble in water, alcohol, ether, and chloroform, but insoluble in carbon bisulphide, has a sp. gr. =  $1.0290$  at  $8^{\circ}$ , and boils at  $238-240^{\circ}$  under 765 mm., at  $150-151^{\circ}$  under 68 mm., and at  $140^{\circ}$  under 30 mm. pressure. It gives the reactions of an alcohol and a nitrile, but does not act on amines or imines. The *ethoxy*-derivative boils at  $185^{\circ}$  and the *acetate* at  $237^{\circ}$ .  $\gamma$ -Chlorobutyronitrile boils at  $195^{\circ}$ , the corresponding *bromo*-derivative at  $213-214^{\circ}$ , and the *iodo*-derivative at  $230^{\circ}$ .

E. W. W.

**Chlorine Derivatives of Nitriles containing Three and Four Carbon Atoms and their Volatility.** By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 22; from *Bull. Acad. roy. Belg.*, [iii], 35, 360-367).— $\alpha$ -Chloropropionitrile, prepared by the action of phosphorus pentachloride on the nitrile of ordinary lactic acid, is a colourless liquid, boils at  $122-123^{\circ}$  under a pressure of 744 mm., and has a sp. gr. =  $1.0792$  at  $10^{\circ}$ .  $\beta$ -Chloropropionitrile, obtained in a similar way from the nitrile of ethylenelactic acid, boils at  $174-176^{\circ}$  under a pressure of 752 mm., and has a sp. gr. =  $1.1443$  at  $18.5^{\circ}$ . The nitriles of  $\alpha$ - and  $\beta$ -hydroxybutyric acid yield  $\alpha$ -chlorobutyronitrile and  $\beta$ -chlorobutyronitrile respectively; the former is a colourless liquid, boils at  $142-143^{\circ}$ , and has a sp. gr. =  $1.0440$  at  $9^{\circ}$ ; the latter boils at  $175-176^{\circ}$ , and has a sp. gr. =  $1.0772$  at  $9^{\circ}$ .  $\gamma$ -Chlorobutyronitrile, prepared by the action of potassium cyanide on trimethylene chlorobromide, boils at  $195^{\circ}$  and has a sp. gr. =  $1.1620$  at  $11^{\circ}$ . The vapour densities of the above compounds were determined, and their boiling points show that the presence of chlorine and nitrogen in a molecule decreases the boiling point, this effect being the most marked when the nitrogen and chlorine atoms are united to the same carbon atom.

E. W. W.

**Alkyl Borates: Properties of Triethylic Borate.** By H. COPAUX (*Compt. rend.*, 1898, 127, 719-722).—When triethylic borate is treated with chlorine in the cold, a gelatinous mass is obtained which carbonises on warming, and yields trichlorether,  $\text{CHCl}_2 \cdot \text{CHCl} \cdot \text{OEt}$ , when hydrolysed with potash. Triethylic borate added to a solution of sodium ethoxide in absolute alcohol produces a crystalline deposit; this compound has the composition  $\text{B}(\text{OEt})_3 \cdot \text{NaOEt}$ , but is not a simple additive product, for it does not regenerate the ethereal salt on heating to  $200^{\circ}$ , neither does it form ether when digested with ethylic iodide at  $140^{\circ}$ . The author suggests that the substance contains quinquivalent boron and has the constitution  $\text{Na} \cdot \text{B}(\text{OEt})_4$ .

G. T. M.

**Compounds of Carbonic Anhydride with Ethylic Ether and Alcohols.** By WALTHER HEMPEL and JOHANNES SEIDEL (*Ber.*, 1898, 31, 2997—3001).—See this vol., ii, 151.

**Conversion of Geraniol into Methylheptenol.** By FERDINAND TRIEMANN (*Ber.*, 1898, 31, 2989—2992).—The substance obtained by Barbier (*Abstr.*, 1898, i, 617) by heating geraniol ("lemonol") with concentrated alcoholic potash at 150° under pressure, and named by him dimethylheptenol, is found to be no other than methylheptenol ("methylhexylenecarbinol"; *Abstr.*, 1894, i, 84; Wallach, *Abstr.*, 1893, i, 598), now formulated as  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ . When linalool is treated in the same way, it is hardly altered.

C. F. B.

**Epidibromohydrins.** By ROBERT LESPIEAU (*Ann. Chim. Phys.*, 1897, [vii], 11, 232—288).—This is a very long paper, consisting, for the most part, of a detailed account of work already published (*Abstr.*, 1893, i, 1; 1896, i, 332; 1898, i, 116). Two isomeric *tribromopropylic alcohols* are described;  $\text{CH}_2\text{Br}\cdot\text{CBr}_2\cdot\text{CH}_2\cdot\text{OH}$ , produced by adding bromine to the alcohol,  $\text{CH}_2\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{OH}$ , forms a syrupy liquid which boils at 125—129° under a pressure of 18 mm.;  $\text{CHBr}_2\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OH}$ , obtained from  $\text{CHBr}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$  (*Abstr.*, 1897, i, 209), resembles its isomeride, and boils at 155—157° under 27 mm. pressure.

*Dibromallylic alcohol*,  $\text{CHBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{OH}$ , which results from the action of sodium methoxide on  $\text{CH}_2\text{Br}\cdot\text{CBr}_2\cdot\text{CH}_2\cdot\text{OH}$ , boils at 205—208° under standard pressure; its *methylic ether*,  $\text{CHBr}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{OMe}$ , boils at 175—177° under 745 mm.; its sp. gr. = 1.903 at 0°.

*Tetrabromopropylic alcohol*,  $\text{CHBr}_2\cdot\text{CBr}_2\cdot\text{CH}_2\cdot\text{OH}$ , produced by adding bromine to the preceding alcohol in chloroform solution, is obtained as a viscid liquid boiling at 164—168° under 20 mm.; its *methylic ether* boils at 140—145° under the same pressure.

*Iodopropargylic alcohol* (iodopropinol),  $\text{Cl}\cdot\text{C}\cdot\text{CH}_2\cdot\text{OH}$ , obtained by the action of a solution of iodine in potassium iodide on the cuprous derivative of propargylic alcohol (propinol), separates from the ethereal extract in colourless, nacreous crystals melting at 43—44°; it turns pink after a time. It is soluble in water, but when boiled with this solvent, undergoes a change, and crystals melting at 150° are obtained. The *methylic ether* melts at 24°, and boils at 74° under 20 mm. pressure.

*Diacetylene glycol* (hexadienediol),  $\text{OH}\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OH}$ , produced by the oxidation of the cuprous derivative of propargylic alcohol with potassium ferricyanide, crystallises in colourless needles melting at 111—112°, and dissolves in all the usual organic solvents except petroleum; it is rapidly coloured on exposure to light, and becomes partly insoluble. A chloroform solution of bromine is rapidly decolorised by the glycol (4Br being absorbed per molecule of glycol). The *diacetyl derivative*, obtained by heating it with acetic anhydride and zinc chloride, melts at 35°. The *dimethylic ether*, prepared from the cuprous derivative of methylic propargylic oxide, is a colourless liquid at ordinary temperatures; it melts at -9°, has a sp. gr. = 0.9969 at 0°, and refraction  $n_D = 1.494$ .

G. T. M.

**A New Sugar accompanying Sorbitol.** By CAMILLE VINCENT and JEAN MEUNIER (*Compt. rend.*, 1898, 127, 760—762).—When sorbitol is obtained from the juice of certain rosaceous fruits, the mother liquor, after the crystallisation of this substance, contains a homologous alcohol not hitherto described. The solution is submitted to the action of the sorbose bacterium, in order to destroy any remaining sorbitol, and then concentrated to a syrupy consistency and treated with benzaldehyde; the *dibenzylidene* compound,  $C_8H_{14}O_8(CHPh)_2$ , of the new alcohol which separates, is insoluble in water, but dissolves in chloroform and alcohol, and crystallises from the former solvent in needles melting at  $230^\circ$ . The *octitol*,  $C_8H_{18}O_8$ , regenerated from the benzylidene compound, is an uncrystallisable syrup which loses 18 per cent. in weight when heated at  $110^\circ$  under reduced pressure; on exposing the desiccated substance to the air for 3 days, 10 per cent. of moisture is regained. Its specific rotation at  $20^\circ$  is  $\alpha_D = -3.42^\circ$ ; the addition of an alkaline solution of borax trebles the rotation without change of sign. The *acetyl* derivative, obtained by heating the syrup with excess of acetic anhydride in the presence of zinc chloride, crystallises from alcohol in tabular crystals and melts at  $119^\circ$ . The physical properties of the new alcohol and its derivatives differ greatly from those of sorbitol and its derivatives, and the paper concludes with a table of comparisons.

G. T. M.

**Rôle of Pentosans in the Manufacture of Crude Sugar.** By ANTON STIFT, and by K. KOMERS and ANTON STIFT (*Bied. Centr.*, 1898, 27, 849—851; from *Oesterr. Zeit. Zuckerind.*, 1897, 1018, and 1898, 6. Compare Abstr., 1898, i, 229).—Extracted diffusion sections of sugar-beet contain considerable amounts of pentosans, only a portion of which passes into the juice. In crude sugar, the pentosans may amount to as much as two-thirds of the organic non-sugar present, but owing to their sparing solubility only a small quantity passes into the green syrup. The pentosans which pass into the juice are not decomposed in the least by the operations employed in purification, &c. It remains uncertain whether the slight reducing power of crude sugar is due to the presence of pentosans, but there certainly seems to be some relation between the amount of pentosans and the reducing power. The amount of sugar in fresh sections changes very quickly; even in one day, the amount of saccharose diminishes considerably, whilst an appreciable amount of invert-sugar is produced.

N. H. J. M.

**Combination of Lithium Chloride with Methylamine.** By J. BONNEFOI (*Compt. rend.*, 1898, 127, 516—519. Compare Abstr., 1897, ii, 37, and this vol., ii, 96).—Methylamine is rapidly absorbed by dry and porous lithium chloride, the composition of the product depending on the temperature.

The compound  $LiCl \cdot NH_2Me$  is formed above  $65^\circ$  by direct combination, or by the action of heat on the other compounds. Its heat of dissolution is + 6.66 Cal., and hence  $LiCl$  sol. +  $NH_2Me$  gas =  $LiCl \cdot NH_2Me$  solid develops + 13.82 Cal. Its vapour pressure is 505 mm. at  $66.2^\circ$ , 642 mm. at  $71^\circ$ , and 819 mm. at  $74.4^\circ$ .

The compound  $\text{LiCl}, 2\text{NH}_2\text{Me}$  is formed between  $40^\circ$  and  $65^\circ$ ; its heat of dissolution is  $+6.647$  Cal., and its heat of formation from its proximate constituents  $+25.88$  Cal. Its vapour pressure is  $149$  mm. at  $27^\circ$ ,  $347$  mm. at  $40^\circ$ , and  $642$  mm. at  $50.2^\circ$ .

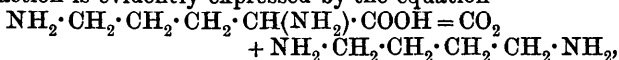
The compound  $\text{LiCl}, 3\text{NH}_2\text{Me}$  is formed below  $40^\circ$ , and no compound containing more methylamine could be obtained even by using the liquefied gas. Its heat of dissolution is  $+7.885$ , and its heat of formation  $+36.69$  Cal. Its vapour pressure is  $289$  mm. at  $22.4^\circ$ ,  $600$  mm. at  $35^\circ$ , and  $827$  mm. at  $40.5^\circ$ .

In all cases, the heat of formation calculated by means of Clapeyron's formula agrees closely with the number directly determined.

The heat of dissolution of methylamine at about  $12^\circ$  is  $+12.05$  Cal.  
C. H. B.

**Formation of Putrescine (Tetramethylenediamine) from Ornithine.** By ALEXANDER ELLINGER (*Ber.*, 1899, 31, 3183—3186).—Ornithine hydrochloride was dissolved in about 100 times its weight of water, and the solution made faintly alkaline with soda and sewn with a little putrefying pancreas; the whole was then left for 3 days at  $30^\circ$ , made faintly acid with acetic acid, heated to boiling, and filtered. The filtrate was shaken with benzoic chloride and soda, when the dibenzoyl derivative of tetramethylenediamine, melting at  $176^\circ$ , was precipitated. The base may also be isolated by Brieger's method, in which case the platinochloride is formed as an intermediate step.

The above mode of preparation of putrescine disposes of Baumann's theory that the substance is produced by an oxidation of ethylamine. The reaction is evidently expressed by the equation



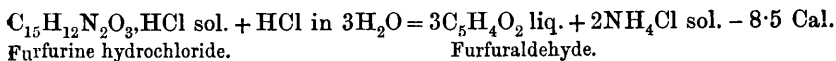
and the production of carbonic anhydride is confirmed by an examination of the gases evolved during the process.  
A. L.

**Amines and Amides Derived from Aldehydes.** By MARCEL DELÉPINE (*Compt. rend.*, 1898, 127, 622—625).—In a series of previous papers (*Abstr.*, 1897, ii, 87, 131, and 359; 1898, i, 363, 415, and 462; ii, 368, 501, and 559), the author has given the thermochemical data involved in the combination between certain aldehydes and ammonia, or certain amines. The data obtained are now classified, and generalisations drawn from them.

I. The interaction of liquid aldehydes with  $1\text{NH}_3$  diss. to form solid derivatives gives rise to less than  $13.7$  Cal. in the case of benzoic, anisic, pyromucic, and acetic aldehydes; from this, it follows that hydrogen chloride, which generates  $13.7$  Cal. in combining with  $\text{NH}_3$  diss., will decompose the derivatives obtained in all these cases into the original aldehyde and ammonium chloride. Experiment verifies this conclusion.

II. The interaction of aromatic aldehydes and aqueous ammonia to form, not the hydramides, but the isomeric glyoxalidines, gives a thermic value  $\approx 17$  Cal., which excludes the possibility of decomposing the bases formed by acids; a study of the salts of furfurine shows that this stability is maintained in presence of very concentrated acids.

Hydrocinnamide, usually classed as a hydramide, is more probably a glyoxalidine. From the equation



it appears that the reverse change, involving the decomposition of ammonium chloride by furfuraldehyde with the formation of furfurine hydrochloride, should be possible. This view was strikingly confirmed by carrying out the analogous decomposition of ammonium chloride by benzaldehyde; this takes place at  $180-185^\circ$ , and gives rise to amarine hydrochloride and aqueous vapour.

III. The elimination of water between an aldehyde and a pyridine or quinoline base is accompanied by a heat development of 15, 30, or 40 Calories; taking into account the fact that the product has a basicity nearly equal to that of the original base, an explanation is afforded of its stability towards hydrolytic agents.

IV. From the heat of formation of hexamethylenetetramine (Abstr., 1897, ii, 359), the latter appears to occupy, as regards stability, a position between the glyoxalidines and the hydramides; like the former, it yields salts with acids, but is decomposed, like the latter, when the proportion or concentration of the acid is increased. This decomposition, however, is limited by the fact that formaldehyde is capable of decomposing ammonium salts (compare *Bull. Soc. Chim.*, 1895, [iii], 13, 163, and Cambier and Brochet, Abstr., 1895, i, 641). In order to isolate the base thus formed, the following systems were studied.

- (1)  $6\text{CH}_2\text{O} + 4\text{NH}_4\text{Cl} + \text{I}_n \text{ in KI } \left. \vphantom{\begin{matrix} 6\text{CH}_2\text{O} + 4\text{NH}_4\text{Cl} + \text{I}_n \text{ in KI} \\ 6\text{CH}_2\text{O} + 4\text{NH}_4\text{I} + \text{I}_4 = 1^{\text{lit.}} \end{matrix}} \right\} \text{Both gave rise to}$
- (2)  $6\text{CH}_2\text{O} + (4\text{NH}_4\text{I} + \text{I}_4 = 1^{\text{lit.}}) \left. \vphantom{\begin{matrix} 6\text{CH}_2\text{O} + 4\text{NH}_4\text{I} + \text{I}_4 = 1^{\text{lit.}} \\ 6 \text{ to } 16\text{CH}_2\text{O} + (4\text{NH}_4\text{I} + \text{HgI}_2 = 1^{\text{lit.}}) \end{matrix}} \right\} \text{C}_6\text{H}_{12}\text{N}_4, \text{CH}_2\text{O}, \text{HI}, \text{I}_3 \text{ to } 4.$
- (3)  $6 \text{ to } 16\text{CH}_2\text{O} + (4\text{NH}_4\text{I} + \text{HgI}_2 = 1^{\text{lit.}}) \left. \vphantom{\begin{matrix} 6 \text{ to } 16\text{CH}_2\text{O} + (4\text{NH}_4\text{I} + \text{HgI}_2 = 1^{\text{lit.}}) \\ 5(\text{C}_6\text{H}_{12}\text{N}_4, \text{CH}_2\text{O}), 6\text{HI}, 4\text{HgI}_2 \end{matrix}} \right\} \text{gave}$
- (4)  $6\text{CH}_2\text{O} + (4\text{NH}_4\text{Cl} + \text{HgCl}_2 = 1^{\text{lit.}}) \left. \vphantom{\begin{matrix} 6\text{CH}_2\text{O} + (4\text{NH}_4\text{Cl} + \text{HgCl}_2 = 1^{\text{lit.}}) \\ 2(\text{C}_6\text{H}_{12}\text{N}_4, \text{CH}_2\text{O}), 2\text{HCl}, 3\text{HgCl}_2 \end{matrix}} \right\} \text{gave}$

$2(\text{C}_6\text{H}_{12}\text{N}_4, \text{CH}_2\text{O}), 2\text{HCl}, 3\text{HgCl}_2$  (m. p. =  $145^\circ$ ).  
In all cases, homogeneous crystals separated; it is remarkable that, in all the compounds formed, the ratio C:N = 7:4. That the compounds obtained are the result of an antagonistic equilibrium is shown by the fact that, on adding  $\text{I}_n + \text{KI}$  to the system  $\text{C}_6\text{H}_{12}\text{N}_4 + 4\text{HCl}$ , the amount of the salt  $\text{C}_6\text{H}_{12}\text{N}_4, \text{CH}_2\text{O}, \text{HI}, \text{I}_n$  obtained is the same as that given by equation (1) alone under similar conditions of concentration. Although the thermic values indicate that formaldehyde should be capable of completely displacing hydrogen chloride in ammonium chloride, this is not the case practically, owing to the fact that hexamethylenetetramine commences to dissociate at  $100^\circ$  into formaldehyde and ammonia.

W. A. D.

**Isomeric Salts of Ethylnitrolic Acid.** By OTTO GRAUL and ARTHUR HANTZSCH (*Ber.*, 1898, 31, 2854—2879).—According to V. Meyer, the nitrolic acids are to be regarded as nitroximes,  $\text{NO}_2 \cdot \text{CR} : \text{N} \cdot \text{OH}$ , and one of their characteristics is the formation of intense red solutions when treated with alkali. The authors have succeeded in isolating these red salts, which they term *erythro*-salts. They correspond with the general formula  $\text{C}_2\text{H}_3\text{N}_2\text{O}_3\text{M}'$ ; they crystallise well, are extremely explosive and unstable, and when treated with dilute acids

are at once reconverted into colourless ethylnitrolic acid. When warmed, or, still better, when placed in direct sunshine, the red salts are converted into a second series of colourless or *leuco*-salts isomeric with the erythro-salts, and a similar change takes place in solution. These leuco-salts cannot be reconverted into the erythro-salts nor yet into the free nitrolic acid, and the acid from which they may be supposed to be derived has not been isolated. Both series of salts undergo practically no hydrolysis in aqueous solution, and they are isomeric, not polymeric. Indications of the existence of a third series of isomeric salts, also colourless, have been met with; they are obtained under certain conditions from the nitrolic acid or from the red salts as amorphous powders, but all attempts to obtain them in a pure form have been unsuccessful, as even below  $0^{\circ}$  they change back into the red salts. A series of intensely yellow salts has also been obtained. These correspond to the general formula  $C_2H_3N_2O_3M' + C_2H_4N_2O_3$ , and may be termed *acid* salts; they are formed by the action of an alkali (1 mol.) on the acid (2 mols.) in concentrated alcoholic solutions and at low temperatures, are very unstable, and in the solid form readily decompose into the red salts and free nitrolic acid. Ethers of the erythro- and leuco-salts can only be obtained by the aid of the silver salts; the ethers obtained from the leuco-silver salts are all oils.

The two isomeric series of salts, erythro- and leuco-, yield the same products on treatment with acid, namely, hydroxylamine, acetic and nitrous acids, and nitrous oxide. The erythro-salts, on treatment with alkalis, yield acetic and nitrous acid, and the leuco-salts, aldehyde. When reduced with sodium amalgam, the erythro-salts and also the free acid yield nitrous acid, ammonia, acetic acid, and azaurolic acid (Abstr., 1883, 40). Under the same treatment, the leuco-salts yield nitrous acid, ammonia, and aldehyde.

Potassium erythronitrolate, when treated at a very low temperature with bromine, yields a blue, unstable oil, which at a somewhat higher temperature becomes converted into Ter Meer's bromodinitroethane (this Journ., 1876, i, 68). The blue compound is considered to be bromonitronitrosoethane,  $NO_2 \cdot CBrMe \cdot NO$ .

The leuco-salts yield yellow or brown bromine derivatives; with an excess of bromine, a compound,  $C_2H_3N_2O_3Br_3$ , is obtained, but this readily loses two atoms of bromine and becomes converted into the yellow solid compound,  $C_2H_3N_2O_3Br$ , which is very sparingly soluble in all ordinary solvents, and is probably a polymeride of the above-mentioned bromonitronitrosoethane.

The authors suggest the following constitutions.

1. Nitroisnitroso-derivatives, free acid, benzoyl derivative, and white, amorphous potassium salt,  $NO_2 \cdot CMe \cdot N \cdot OR$ .

2. Isonitronitroso-derivatives, the stable leuco-salts,  $NO \cdot CMe \cdot NO_2M'$ .

3. Erythro-salts,  $CMe \begin{array}{c} \text{N} \\ \text{---} \\ \text{NO(OM')} \end{array} > O$ , and arguments in favour of these constitutions are given in detail.

Ethylnitrolic acid itself is a very feeble acid, and may be compared with phenol or acetophenoneoxime. The erythro-salts are derivatives of a much stronger acid and undergo little or no hydrolysis in aqueous

solution; the following have been prepared, *potassium, sodium, silver, lead, and mercuric erythronitrolates.* J. J. S.

**The Rendering Active ("Activirung") of Oxygen. Part III. Oxidation of Triethylphosphine.** By CARL ENGLER and J. WEISSBERG (*Ber.*, 1898, 31, 3055—3059).—The peroxide of turpentine has been shown (this vol., i, 221) to be destroyed at 140—160°, further oxidation of the turpentine taking place, and it is probable that a similar secondary action occurs at ordinary temperatures in the case of triethylphosphine, so that the oxidising action of the initial product is only observed after all free triethylphosphine has disappeared; once the activity is manifested, however, it is more or less permanent. It is shown, by means of tests similar to those used in the case of the product from turpentine, that the oxidising power is not due to hydrogen peroxide or ozone.

The authors have examined the products of the action of dry oxygen on triethylphosphine. The crude liquid deposits crystals at  $-10^\circ$ , or forms a solid, crystalline mass; the crystals have the composition of triethylphosphine oxide,  $\text{POEt}_3$ , whilst the liquid seems to be a mixture of ethylic diethylphosphinate,  $\text{POEt}_2\cdot\text{OEt}$ , with diethylic ethylphosphinate,  $\text{POEt}(\text{OEt})_2$ , and, possibly, also triethylic phosphinate,  $\text{PO}(\text{OEt})_3$  (compare Jorissen, *Abstr.*, 1897, ii, 253). When the liquid is hydrolysed with baryta water, an odour of triethylphosphine is noticeable, whilst alcohol and aldehyde-like substances may be driven over by distillation; the non-volatile portion, on evaporation, deposits the pure barium salt of diethylphosphinic acid and an impure salt of monethylphosphinic acid.

The initial stage of the oxidation is supposed to be the formation of the peroxide,  $\text{O} \begin{array}{c} \diagup \diagdown \\ \text{P} \end{array} \text{Et}_3$ , which then suffers isomeric change, or reacts with unaltered triethylphosphine.

The analyses of the crude autoxidation product confirm the authors' original observation that rather less than one molecular proportion of oxygen is absorbed. This is not in agreement with the results of Jorissen (*loc. cit.*), but the discrepancy is, no doubt, due to the higher temperatures employed by that chemist. A. L.

**Identity of the four Affinities of Sulphur in Sulphines.** By A. BRUCHONENKO (*Ber.*, 1899, 31, 3176—3182).—Feebly active ethylic isoamylic sulphide ( $[\alpha]_D = +3.41$  at  $18.5^\circ$ ) was treated with a molecular proportion of methylic iodide at ordinary temperatures. The *methylethylisoamylsulphine iodide*,  $\text{C}_5\text{H}_{11}\cdot\text{SMeEtI}$ , thus formed, was obtained in the form of regular, transparent needles; it decomposed spontaneously, even when kept in a vacuum and in the dark; when treated with cold nitric acid, it lost iodine, but did not yield sulphuric acid when heated with fuming nitric acid at 170—180° during several hours. It was optically active, its specific rotation being  $[\alpha]_D = +4.88$  at  $18^\circ$ , and it gave a thick, oily precipitate with cadmium iodide.

Active *methylethylamylsulphine iodide*,  $\text{C}_5\text{H}_{11}\cdot\text{SMeEtI}$ , was made by two different methods, namely, by the action of methylic iodide on ethylic amylic sulphide ( $[\alpha]_D = +14.71$  at  $19^\circ$ ), and by the action of ethylic iodide on methylic amylic sulphide ( $[\alpha]_D = +13.24$  at  $20^\circ$ ). In both

cases, the substance was obtained as a semi-crystalline syrup, soluble in water and alcohol, but insoluble in ether and benzene, and having a specific rotation  $[\alpha]_D = 13.9$  at  $19^\circ$ ; the concentration of the solution was found to have little effect on the rotatory power.

As the preparation of these two substances has been carried out under conditions which render the occurrence of any isomeric change improbable, their identity may be regarded as further evidence of the equality of the four affinities of sulphur.

The proximity of the rotatory powers of the sulphides and the derived sulphine iodides would lead to the surmise that the latter are monomolecular, and this supposition is confirmed by determinations of their molecular weights. A. L.

**Derivatives of Natural Methylheptenone.** By GEORGES LÉSER (*Compt. rend.*, 1898, 127, 763—764. Compare Abstr., 1898, i, 617).—When a mixture of ethylic acetate and methylheptenone is treated with sodium and the product distilled under a pressure of 15—16 mm., the lower fraction boiling at  $115^\circ$  consists of acetylmethylheptenone, whilst that distilling between  $130^\circ$  and  $200^\circ$  contains a substance, produced by the condensation of two molecules of methylheptenone, accompanied by an elimination of one molecule of water, to which the name *bis-methylheptenone* is provisionally given; it boils at  $172$ — $174^\circ$  under a pressure of 16 mm.

*Acetylmethylethylheptenone* results from the action of ethylic iodide on the sodium derivative of acetylmethylheptenone in alcoholic solution; it boils at  $133$ — $135^\circ$  under a pressure of 15 mm. *Methylnone-none*,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Et}$ , produced by boiling the preceding compound with aqueous potash, boils at  $203$ — $205^\circ$  under ordinary pressure. *Ethylic methylhexenonepyruvate* (ethylic 2-methyl-6:8-dione-2-noneoate),  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOEt}$ , formed on mixing together alcoholic solutions containing molecular proportions of methylheptenone, ethylic oxalate, and sodium ethoxide, is obtained in the form of its copper derivative,  $\text{Cu}(\text{C}_{12}\text{H}_{17}\text{O}_4)_2$ , which separates in olive-green needles when the crude product is added to a solution of copper acetate. The ethereal salt, obtained on decomposing the copper derivative with dilute sulphuric acid, boils at  $164$ — $165^\circ$  under a pressure of 16 mm. G. T. M.

**Direct Oxidation of Fat.** By MAURICE HANRIOT (*Compt. rend.*, 1898, 127, 561—563).—When ozone is passed over neutral fat, an increase of 23 per cent. in the weight of the latter occurs; acetic acid appears to be formed in small quantity, together with other fatty acids which were not identified; formic acid, however, is not formed, or oxalic acid, sugar, starch, or cellulose. No details of the nature of the fat employed are given. W. A. D.

**Conversion of Geranic Acid into Citronellic Acid.** By FERDINAND TIEMANN (*Ber.*, 1898, 31, 2899—2903).—The synthesis of methylheptenone,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ac}$ , and of geranic acid has already been described (Abstr., 1894, i, 84), and also the conversion of geranic acid into terpenes and their derivatives (*ibid.*, 1895, i, 639).

Geranic acid,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOH}$ , is not reduced to citronellic acid,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COOH}$ , when



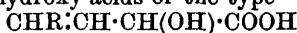
boiled with water and sodium amalgam, but is reduced when sodium (20 grams) is added to a solution of geranic acid (20 grams) in boiling amyl alcohol. The yield of citronellic acid is over 60 per cent.

Citronellonitrile, obtained from citronellaldoxime, is not readily hydrolysed by alcoholic potash; when boiled for 5–6 hours with a 15 per cent. alkaline solution, and then diluted with water, *citronellamide* is precipitated; it crystallises from light petroleum in colourless needles melting at 81.5–82.5°, and is only sparingly soluble in water, but dissolves readily in most organic solvents.

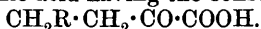
Citronellaldehyde is obtained when a mixture of calcium formate and citronellate is strongly heated; the yield is not good.

J. J. S.

**Transformation of Unsaturated  $\alpha$ -Hydroxy-acids into Hydrofurfurancarboxylic Acids.** By RUDOLPH FITTIG (*Annalen*, 1898, 303, 165–171. Compare Abstr., 1898, i, 196).—It has been shown by the author that hot, dilute hydrochloric acid or caustic soda transforms unsaturated  $\alpha$ -hydroxy-acids of the type



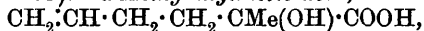
into the isomeric  $\alpha$ -ketonic acid having the constitution



It was not found possible to trace the intermediate stages of the change, and, in order to gain information on this point, the author has studied the behaviour of an acid in which the ethylenic linking is further removed from the carboxylic group. The results are described in the following abstract.

M. O. F.

**Methylallyllactic Acid and Dimethylhydrofurfurancarboxylic Acid.** By RUDOLPH FITTIG and HAROLD DE HAVEN-BOYD (*Annalen*, 1898, 303, 171–183).— *$\alpha$ -Methylallyllactic acid*,



produced by hydrolysing the nitrile obtained from allylacetone and hydrogen cyanide, is a colourless, viscous liquid which decreases slightly in weight when preserved in a vacuum, probably owing to the formation of anhydride. The *calcium* salt crystallises in white leaflets containing  $1\frac{1}{2}\text{H}_2\text{O}$ ; it dissolves more readily in cold water than in hot. The *barium* salt crystallises in anhydrous needles; the *silver* salt is very readily soluble in water. The *amide* crystallises in large, colourless, monoclinic plates and melts at 71°. The acid resists the action of sodium amalgam, and of boiling aqueous soda.

*$\alpha$ -Methyldibromo- $\beta$ -propyllactic acid*,

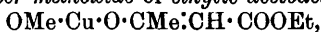


obtained by adding bromine to the foregoing acid dissolved in chloroform, crystallises in colourless prisms and melts at 107°.

*Dimethylhydrofurfurancarboxylic acid*,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{COOH}$ , prepared by heating calcium methylallyllactate with hydrochloric acid, is a colourless, volatile liquid which boils at 228°. The *calcium* salt contains  $2\text{H}_2\text{O}$ , and the *barium* and *silver* salts are anhydrous. The acid is indifferent towards sodium amalgam, and does not unite with bromine. On distilling an intimate mixture of the calcium salt with lime, methyl butyl ketone is obtained.

M. O. F.

**Basic Copper Compounds of Ethylic Acetoacetate and Ethylic Benzoylacetate.** By WILHELM WISLICENUS (*Ber.*, 1898, 31, 3151—3158).—Ethylic cupro-acetoacetate can be advantageously prepared by agitating an ethereal solution of ethylic acetoacetate with copper acetate solution. The copper compound crystallises from benzene in green needles, and melts at 192—193°, whereas Conrad (*Abstr.*, 1878, 26) gives the melting point as 182°. When the copper compound is boiled with methylic alcohol, ethylic acetoacetate is set free, and a *basic copper methoxide of ethylic acetoacetate*,

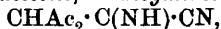


is produced, which crystallises from methylic alcohol in small, blue needles and melts and decomposes between 156° and 175°. The reaction is not complete, but leads to a state of equilibrium between the green and blue salts, which is largely influenced by the relative proportions of ethylic acetoacetate and methylic alcohol present. The blue compound is reconverted into the green salt when it is warmed with an equivalent of ethylic acetoacetate. The same change occurs when the blue compound is boiled with benzene, and it is probable that, in this case, cupric methoxide,  $\text{Cu}(\text{OMe})_2$ , is also produced. Ethylic cuprobenzoylacetate, which melts at 182—183°, also undergoes a similar change when boiled with methylic alcohol, a *basic methoxide* being produced which crystallises in blue, microscopic needles.

A. H.

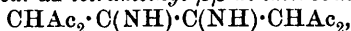
**Action of Cyanogen on Ethylic Acetoacetate and Acetylacetone.** By WILHELM TRAUBE (*Ber.*, 1898, 31, 2938—2946. Compare *Abstr.*, 1898, i, 241).—When cyanogen is passed into a well-cooled alcoholic solution of ethylic acetoacetate containing only a small amount of sodium ethoxide, a crystalline precipitate is produced which consists of *ethylic  $\alpha$ -acetyl- $\beta$ -cyano- $\beta$ -imidopropionate*, or *ethylic dicyanacetoacetate*,  $\text{NH} \cdot \text{C}(\text{CN}) \cdot \text{CHAc} \cdot \text{COOEt}$ , melting at 122°; this substance has acid properties and dissolves in alkalis, but the solutions rapidly decompose, ethylic cyanacetoacetate, melting at 36°, being formed. If the alcoholic solution of ethylic acetoacetate is not cooled during the treatment with cyanogen, *ethylic  $\alpha\alpha$ -diacetyl- $\beta\beta$ -di-imido-adipate*, or *ethylic dicyanodiacetoacetate*,  $\text{C}_2(\text{NH})_2(\text{CHAc} \cdot \text{COOEt})_2$ , is produced, and the latter is also formed by the action of ethylic acetoacetate and a little sodium ethoxide on the foregoing compound. It crystallises in colourless needles, melts at 132°, and dissolves in aqueous soda, forming a yellowish-red solution, from which acids precipitate *monethylic di-imidoacetylmethylcyclopentenedicarboxylate*,  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_5$ , which crystallises in dark yellow needles melting at 136°. Ethylic dicyanacetoacetate is converted by ethylic malonate, in the presence of a small amount of sodium ethoxide, into *ethylic  $\alpha$ -carboxyl- $\alpha'$ -acetyl- $\beta\beta$ -di-imido-adipate*,  $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_7$ , which forms compact crystals melting at 93°.

*Cyanimidomethylacetylacetone*, or *dicyanacetylacetone*,



prepared in a similar manner to the corresponding derivative of ethylic acetoacetate, crystallises in plates melting at 129—131°. Its solution in aqueous soda readily decomposes, forming *cyanacetylacetone*,  $\text{CHAc}_2 \cdot \text{CN}$ ,

which crystallises in large, colourless plates melting at  $50^{\circ}$ , and is a strong acid, decomposing carbonates and acetates. *Dicyanodiacetylacetone*, or *symmetrical aa-tetramethyl- $\beta\beta$ -di-imidobutane*,



which can also be obtained in a similar manner to the corresponding derivative of ethylic acetoacetate, crystallises in pale yellow tablets melting at  $147^{\circ}$ . It is decomposed by hot water with formation of

*di-imidotriacetylmethylcyclopentene*,  $\text{CMe} \begin{smallmatrix} \swarrow \text{CAc} \cdot \text{C} \cdot \text{NH} \\ \searrow \text{CAc}_2 \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$ , which forms

colourless crystals melting at  $194$ – $198^{\circ}$ . Dicyanacetylacetone is converted by ethylic acetoacetate, in presence of a small amount of sodium ethoxide, into *ethylic di-imidodiacetylmethylcyclopentenecarboxylate*,  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4$ , which melts at  $153$ – $158^{\circ}$ . Dicyanacetylacetone is, moreover, converted by alcohol containing a small amount of sodium ethoxide into a substance which forms well-developed, yellowish-green crystals melting at  $162^{\circ}$ , and is probably *di-imidodiacetyltrimethylene*,

$\text{CAc}_2 \begin{smallmatrix} \swarrow \text{C} \cdot \text{NH} \\ \searrow \text{C} \cdot \text{NH} \end{smallmatrix}$ . When cyanogen is passed into an alcoholic solution of

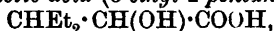
ethylic malonate containing a small amount of sodium ethoxide, a red sodium salt, which has previously been described, separates, whilst the filtrate contains *ethylic dicyanomalonate* or *ethylic cyanimidoisuccinate*,  $\text{NH} \cdot \text{C}(\text{CN}) \cdot \text{CH}(\text{COOEt})_2$ ; this crystallises in colourless needles, and melts at  $93^{\circ}$ . A. H.

**Derivatives of Ethylic Diethylacetoacetate.** By MAX CONRAD and RICHARD GAST (*Ber.*, 1898, 31, 2954–2957).—*Ethylic  $\gamma$ -bromodiethylacetoacetate*,  $\text{CH}_2\text{Br} \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{COOEt}$ , obtained by treating ethylic diethylacetoacetate with the requisite quantity of bromine, is a colourless oil which boils at  $245$ – $255^{\circ}$ , but at the same time undergoes partial decomposition, evolving hydrogen bromide. When boiled for some 15–20 hours with an alcoholic solution of potassium acetate, it yields the *acetate*,  $\text{OAc} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{COOEt}$ , boiling at  $255$ – $265^{\circ}$  and having a sp. gr. = 1.058 at  $15^{\circ}/15^{\circ}$ . When kept for 12 months, it decomposes into ethylic acetate and the *lactone* of

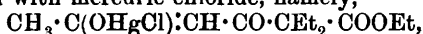
*$\gamma$ -hydroxydiethylacetoacetic acid*,  $\text{O} \begin{smallmatrix} \swarrow \text{CH}_2 \cdot \text{CO} \\ \searrow \text{CO} - \text{CEt}_2 \end{smallmatrix}$ , boiling at  $219$ – $225^{\circ}$ .

The acetate mentioned above yields an oily *monobromo-derivative*, which, when boiled for several hours with baryta water, is converted into  *$\beta$ -diethylmalic acid*,  $\text{COOH} \cdot \text{CH}(\text{OH}) \cdot \text{CEt}_2 \cdot \text{COOH}$ , which melts at  $117^{\circ}$ .

*$\beta$ -Diethylethylidenelactic acid (3-ethyl-2-pentanololic acid)*,



is obtained when the acetate is hydrolysed by boiling with dilute sulphuric acid for several days; it melts at  $82^{\circ}$  and yields a crystalline *silver salt* readily soluble in warm water. Just as ethylic dimethylacetoacetate, when treated with sodium, yields ethylic isobutyrate and ethylic sodio- $\gamma$ -acetyldimethylacetoacetate (*Abstr.*, 1898, i, 512), so ethylic diethylacetoacetate yields *ethylic sodio- $\gamma$ -acetyldiethylacetoacetate*,  $\text{CH}_3 \cdot \text{C}(\text{ONa}) \cdot \text{CH} \cdot \text{CO} \cdot \text{CEt}_2 \cdot \text{COOEt}$ . This is best isolated in the form of its compound with mercuric chloride, namely,



which can be recrystallised from ethylic acetate, and then melts at  $152^{\circ}$ . Free *ethylic  $\gamma$ -acetyldiethylacetate* (ethylic 2:2-diethyl-3:5-hexanedionate, or, according to Collie, ethylic  $\alpha$ -diethyltriacetate) is obtained when the mercury derivative is treated with hydrogen sulphide and then extracted with ether; it is a yellowish oil, has feebly acid properties, and, when shaken with copper acetate solution, yields a crystalline *copper* derivative,  $(C_{12}H_{19}O_4)_2Cu$ , which, after recrystallisation from light petroleum, melts at  $82^{\circ}$ . J. J. S.

**Tautomerism: Desmotropy of 2-Acetylangelicalactone.** By LUDWIG KNORR and WILLIAM AUGUSTUS CASPARI (*Annalen*, 1898, 303, 133—149).—On heating ethylic diacetosuccinate, ethylic isocarbopyrotritarate,  $COOEt \cdot C \begin{smallmatrix} \swarrow C(:CMe \cdot OH) \cdot CO \\ \searrow CMe \text{-----} O \end{smallmatrix}$ , is obtained (Abstr., 1894, i, 360). The authors find that when the free acid is distilled, carbonic anhydride is eliminated, and the two desmotropic 2-acetyl-angelicalactones produced; these are distinguished as the  $\alpha$ -lactone and the  $\beta$ -lactone respectively.

*$\alpha$ -2-Acetylangelicalactone*,  $CH \begin{smallmatrix} \swarrow C(:CMe \cdot OH) \cdot CO \\ \searrow CMe \text{-----} O \end{smallmatrix}$ , the enolic form, is obtained in a highly purified condition on distilling the  $\beta$ -modification; it crystallises from ether in long, colourless prisms, melts at  $63^{\circ}$ , and boils at  $150^{\circ}$ ,  $159^{\circ}$ , and  $216^{\circ}$  under pressures of 45 mm., 100 mm., and 760 mm. respectively. It dissolves sparingly in water, which becomes acid. The lactone reduces ammoniacal silver nitrate and the chlorides of mercury and gold; with alcoholic ferric chloride, it develops a characteristic cornflower-blue coloration which, after an interval, becomes violet, and, finally, red. Exposure to air causes the lactone to deliquesce, oxidation converting it into a yellow resin which dissolves readily in organic media and develops a deep red coloration with ferric chloride; a certain amount of the  $\beta$ -modification is also produced. The *sodium* derivative is obtained by boiling a benzene solution of either isomeride with sodium wire in a reflux apparatus; it is a colourless, amorphous powder, becoming reddish when exposed to air, and dissolves with extraordinary readiness in alcohol and in water. Dilute mineral acids precipitate the  $\alpha$ -lactone from concentrated aqueous solutions of the sodium derivative, but carbonic anhydride yields chiefly the isomeride, which is precipitated exclusively from dilute solutions by this agent; numerous metallic salts give rise to derivatives when added to moderately concentrated solutions of the sodium derivative. The *iron* derivative forms an indigo-blue, crystalline powder, and contains  $4H_2O$ ; the *barium* derivative is crystalline, and also contains  $4H_2O$ . The *phenylurethane* melts at  $102^{\circ}$ . Concentrated sulphuric acid dissolves the  $\alpha$ -lactone, and on pouring the liquid into water, pyrotritaric acid is produced. Diazomethane also acts on the lactone, forming a liquid which decomposes on distillation; as the substance does not develop colour with ferric chloride, it is probably the methyl ether of the lactone.

*$\beta$ -2-Acetylangelicalactone*,  $CH \begin{smallmatrix} \swarrow CH(CO \cdot Me) \cdot CO \\ \searrow CMe \text{-----} O \end{smallmatrix}$ , the ketonic form, crystallises from chloroform or glacial acetic acid in white leaflets and

melts indefinitely at  $177-180^{\circ}$ ; at  $20^{\circ}$ , 1 part dissolves in 49.5 parts of chloroform, 121 parts of acetone, 296 parts of alcohol, 544 parts of benzene, or 3948 parts of ether. The  $\beta$ -lactone has reducing properties resembling those of the isomeride, but it does not develop colour with ferric chloride; it is indifferent to the action of air. The lactone dissolves slowly in dilute caustic soda, and yields a crystalline sodium derivative with the concentrated alkali; from freshly prepared solutions, mineral acids precipitate the unchanged substance, but if an interval has elapsed since the solution was formed, a certain amount of the  $\alpha$ -lactone is obtained along with it, this being the exclusive product after the alkaline solution has been boiled. Concentrated sulphuric acid dissolves the lactone, and yields it unchanged if poured immediately into water, but if this operation is performed after an interval of 8 hours, pyrotartaric acid is obtained; protracted treatment with boiling water eliminates carbonic anhydride, and converts the lactone into acetonylacetone. Phenyllic cyanate and diazomethane are without action on the  $\beta$ -lactone.

The conditions under which the two lactones are interconvertible are stated in the paper. In general, a low temperature favours the production of the ketonic modification. M. O. F.

**Polyaspartic Acids.** By HUGO SCHIFF (*Annalen*, 1898, 303, 183—217. Compare Abstr., 1898, i, 67).—This paper contains experimental details relating to the former communication (*loc. cit.*). Whilst octaspartide combines with 8 mols. of phenylhydrazine, tetraspartide yields the *triphenylhydrazide*,  $C_{34}H_{38}N_{10}O_9$ , and the *tetraphenylhydrazide*,  $C_{40}H_{46}N_{12}O_9$ .

Octaspartide dissolves in aniline, forming anilides in which 3, 4, 6, or 8 aniline residues have combined with the corresponding number of carbonylic groups. Those derivatives in which fewer than 8 aspartide rings have been resolved are capable of further action with bases. Octaspartide *trianilide*,  $C_{50}H_{47}N_{11}O_{17}$ , is a greyish powder which becomes yellow at  $90^{\circ}$ , softens at about  $245^{\circ}$ , and decomposes as it melts. The *tetranilide*,  $C_{56}H_{54}N_{12}O_{17}$ , decomposes and evolves gas at  $230-240^{\circ}$ ; it dissolves in phenylhydrazine, forming the tetraphenylhydrazide,  $C_{80}H_{86}N_{20}O_{17}$ , which becomes brown at about  $190^{\circ}$  and completely fused at  $210^{\circ}$ , when it decomposes. The *hexanilide*,  $C_{68}H_{68}N_{14}O_{17}$ , becomes brown at about  $90^{\circ}$ , and decomposes at  $125^{\circ}$ ; the *octanilide*,  $C_{80}H_{82}N_{16}O_{17}$ , decomposes at about  $130^{\circ}$ .

Further action of boiling aniline converts the octaspartanilides into phenyloctaspartanilides, with elimination of ammonia. *Triphenyloctaspartooctanilide*,  $C_{98}H_{94}N_{16}O_{17}$ , *tetraphenyloctaspartooctanilide*,  $C_{104}H_{98}N_{16}O_{17}$ , and *pentaphenyloctaspartooctanilide*,  $C_{110}H_{102}N_{16}O_{17}$ , melt somewhat indefinitely at  $120-125^{\circ}$ ,  $170^{\circ}$ , and  $160^{\circ}$  respectively.

Tetraspartide behaves towards aniline like octaspartide. The *dianilide*,  $C_{28}H_{28}N_8O_9$ , decomposes at  $270-275^{\circ}$  without undergoing fusion, whilst the *trianilide*,  $C_{34}H_{35}N_7O_9$ , melts indefinitely at  $245-260^{\circ}$ . The *tetranilide*,  $C_{40}H_{42}N_8O_9$ , softens at about  $220^{\circ}$ , and decomposes above  $235^{\circ}$ ; the *phenyltetranilide*,  $C_{46}H_{46}N_8O_9$ , is a brownish-yellow powder which melts and decomposes at  $130^{\circ}$ .

The action of aniline on aspartic acid has also been investigated. M. O. F.

**Conversion of Trimethylene into Propylene.** By ALESEI A. WOLKOFF and BORIS N. MENSCHUTKIN (*Ber.*, 1898, 31, 3067—3073. Compare Tanatar (*Abstr.*, 1896, i, 457).—Pure trimethylene is best obtained by heating trimethylenic bromide (10 grams), zinc dust (12.5 grams), and 96 per cent. alcohol (20 c.c.) in a reflux apparatus at 70—80°, and passing the evolved gas through two wash-bottles containing bromine, then through sodium hydroxide solution and finally through a 0.5 per cent. solution of potassium permanganate, which should not become decolorised. It has been shown that trimethylene obtained by Gustavson's method always contains propylene, the amount varying between 13 and 39.5 per cent.; this can only be completely removed by passing the gas through bromine, when a small amount of the trimethylene is also absorbed. Tanatar's experiments have been repeated, pure trimethylene free from propylene being employed, and it has been found that when the purified gas is passed through a tube heated to dull redness, no trace of propylene is formed. A little oxymethylene is obtained, its formation being seemingly due to small amounts of air from the drying apparatus. Tanatar's results must be due to the fact that he employed trimethylene containing propylene. Experiments made at higher temperatures indicate that the products formed are ethylene, paraffin hydrocarbons, and hydrogen. Trimethylenic bromide is not converted into propylenic bromide by the action of zinc bromide, but yields *ethylic α-bromopropylic ether*,  $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OEt}$ , boiling at 147—148°, and having a sp. gr. = 1.2597 at 0°. This brom-ether, when treated with zinc-dust and alcohol, gives a nearly theoretical yield of propylene at 60—70°, together with a small quantity of ethylic allylic ether boiling at 67—72°. Allylic bromide, when treated in alcoholic solution with zinc dust, yields propylene. It seems probable then that the conversion of trimethylene into propylene is due to the following reactions. Trimethylenic bromide → ethylic α-bromopropylic ether → allylic ethylic ether → allylic bromide → propylene. J. J. S.

**1:4-Dimethylhexamethylene.** By NICOLAI D. ZELINSKY and S. NAUMOW (*Ber.*, 1898, 31, 3206—3208).—Ethylic dimethylsuccinylsuccinate, when hydrolysed with dilute sulphuric acid, yields two stereoisomeric dimethyldiketoexamethylenes, the one, previously described by Baeyer (*Abstr.*, 1892, 1183), melting at 93°, and a second crystallising from water in needles and melting at 115—117°. The mixture of the two ketones, when reduced according to Baeyer's method for the synthesis of quinitol (*ibid.*, 1833), yields a syrupy mass of dimethylquinitol, which, when further treated with 4—5 times its volume of concentrated hydrobromic acid at 100°, yields two stereoisomeric *dibromides*, the one an oil, and the other melting at 93—94°. The *di-iodide* of dimethylquinitol may be obtained in a similar manner, and when reduced by the zinc-palladium process (see this vol., i, 181) yields a hydrocarbon boiling at 118—119°. In the crude form, it has an aromatic odour, but this disappears on treatment with con-

centrated sulphuric acid. From its method of formation, this hydrocarbon must be 1:4-dimethylhexamethylene or hexahydroparaxylylene. The boiling point found does not agree with that previously given by Schiff (Abstr., 1880, 892). When treated with bromine in the presence of aluminium bromide, Jacobsen's tetrabromoparaxylylene is obtained. Hexahydroparaxylylene differs but little in boiling point and specific gravity from the previously described hexahydrometaxylylene.

J. J. S.

**Fluorine Derivatives of Toluene.** By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1898, ii, 26—27; from *Bull. Acad. roy. Belg.*, [iii], 35, 375—420).—When a mixture of benzotrichloride with two-thirds of its weight of antimony fluoride is heated quickly and boiled for 5 minutes, *o*-difluorochlorotoluene,  $\text{C}_6\text{H}_4\text{Cl}_2\text{F}_2$ , and *o*-trifluorotoluene,  $\text{C}_6\text{H}_4\text{F}_3$ , are obtained. The former is a colourless liquid, boils at  $142.6^\circ$  under a pressure of 770 mm., has a sp. gr. = 1.25445 at  $13^\circ$ , and a specific refractive index = 1.46969; the latter is a colourless liquid, boils at  $103.5^\circ$ , has a sp. gr. = 1.19632 at  $14^\circ$ , and a specific refractive index = 1.41707. Trifluorotoluene is not decomposed at high temperatures, and not attacked by water, alkalis, phenols, aniline, reduced copper, or phenylhydrazine; with fuming nitric acid, it yields *o*-trifluorometanitrotoluene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CF}_3$ , which boils at  $201.5^\circ$ , has a sp. gr. = 1.43571 at  $15^\circ$ , and a specific refractive index = 1.47582; this is reduced by stannous chloride and hydrochloric acid to *o*-trifluorometatoluidine, which boils at  $187.5^\circ$ , has a sp. gr. = 1.30467 at  $12.5^\circ$ , and a specific refractive index = 1.4847; the hydrochloride and nitrate were prepared. By the action of acetic anhydride on trifluorotoluidine, acetotrifluorotoluidide is obtained; it crystallises from water in needles, melts at  $103^\circ$ , and boils at  $287^\circ$ . Trifluorometatoluitrile,  $\text{CF}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CN}$ , prepared by means of the diazo-compound, melts at  $14.5^\circ$ , boils at  $189^\circ$ , has a sp. gr. = 1.28126 at  $20^\circ$ , a specific refractive index = 1.45048, and when hydrolysed yields isophthalic acid and trifluorometatoluic acid,  $\text{CF}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ ; the latter crystallises from chloroform in needles, melts at  $103^\circ$ , boils at  $238.3^\circ$  under a pressure of 770 mm., and yields crystalline sodium, silver, lead, and barium salts. The physical constants of the above fluorine derivatives were determined.

E. W. W.

**Influence of Light on Chemical Substitution.** By CORNELIUS RADZIEWANOWSKI and JULIAN SCHRAMM (*Chem. Centr.*, 1898, i, 1019—1020; from *Akad. Wiss. Krakau*, 1898, Februarheft, 61—68).—By the action of chlorine (1 mol.) on *ortho*-xylene (1 mol.) in sunlight, *ortho*-xylylic and *ortho*-xylylenic chlorides are formed; the former boils at  $195$ — $203^\circ$ , the latter crystallises in long prisms, melts at  $55^\circ$ , boils at  $240$ — $260^\circ$ , and constitutes the main portion of the product when twice the above quantity of chlorine is used. The fractions of higher boiling point yield *ortho*-xylene hexachloride,  $\text{C}_6\text{H}_4\text{Me}_2\text{Cl}_6$ , which forms rhombic crystals, melts at  $194.5^\circ$ , and boils at  $260$ — $265^\circ$ ; it is soluble in benzene, chloroform, and carbon bisulphide, but insoluble in alcohol and ether. By the action of chlorine on paraxylylene in sunlight, *paraxylylic* and *paraxylyl-*

*enic chlorides* are obtained; the former boils at 200—202°, the latter crystallises in rhombic plates and melts at 100°. Metaxylylene yields a mixture of metaxylylic chloride and chlorometaxylylene with some *metaxylylenic chloride*. Substances containing more side chains in the meta-position are apparently not so susceptible to the influence of light as regards the action of chlorine, for chlorine and bromine do not attack mesitylene as readily as metaxylylene. In the product obtained by the action of chlorine (2 mols.) on ethylbenzene in sunlight, *dichlorethylbenzene*,  $\text{CCl}_2\text{MePh}$ , was detected by the formation of acetophenone when heated with silver oxide; substitution also occurs to some extent in the benzene ring. E. W. W.

**Action of Mercuric Chloride on Aqueous Phenol Solutions.** By BRUNO GRÜTZNER (*Arch. Pharm.*, 1898, 236, 622—626).—When a saturated solution of mercuric chloride in a 5 per cent. aqueous solution of phenol is heated to boiling and then allowed to cool, *hydroxyphenyl-mercury chloride*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{HgCl}$ , separates in mossy crystals, soluble with difficulty in alcohol, and almost insoluble in benzene, chloroform, and light petroleum.

The author has, however, abandoned the investigation of this substance, owing to Dimroth's work (this vol., i, 54) in the same direction. A. W. C.

**Constitution and Cryoscopic Behaviour of Orthocyanophenols.** By KARL AUWERS and A. J. WALKER (*Ber.*, 1898, 31, 3037—3045).—It has been shown that phenols containing a negative substituent in the ortho-position relatively to the hydroxyl group exhibit normal cryoscopic behaviour, that of the corresponding meta- and para-compounds being abnormal (compare Abstr., 1896, ii, 293); orthocyanophenol is the only exception which has been hitherto observed, and the desmotropic formula,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \\ \text{C} : \text{NH} \end{smallmatrix}$ , was suggested by Victor Meyer to account for the peculiarity. The authors consider, however, that the chemical and cryoscopic behaviour of the substance is incompatible with this supposition, and the abnormal value of the molecular weight remains unexplained.

The *ammonium* derivative of orthocyanophenol melts at 139—141°, evolving ammonia; the *silver* derivative becomes dark under the influence of light. The *benzylic ether*, whether prepared from the silver derivative and benzylic iodide in benzene, or from the sodium derivative and benzylic chloride in alcohol, crystallises from petroleum in white needles, and melts at 71—72°. The *oxime* of benzylsalicylaldehyde crystallises from petroleum in white leaflets, and melts at 71.5°; boiling acetic anhydride converts it into the benzylic ether of orthocyanophenol.

The *benzylic ether* of paracyanophenol separates from petroleum in white needles, and melts at 94—94.5°.

The *oxime* of the benzylic ether of parahydroxybenzaldehyde melts at 110—111.5°, and yields the benzylic ether of paracyanophenol under the influence of boiling acetic anhydride.

*Bromocyanophenol* [ $\text{OH} : \text{CN} : \text{Br} = 1 : 2 : 4$ ], prepared from the oxime



of bromosalicylaldehyde, crystallises from benzene or dilute alcohol, and melts at 158—159°. *Dibromocyanophenol*  $[\text{OH}:\text{CN}:\text{Br}_2 = 1:2:4:6]$ , produced by the direct action of bromine on orthocyanophenol, crystallises from a mixture of benzene and petroleum in silky needles, and melts at 167—168°; prisms melting at the same temperature are obtained by using alcohol or benzene, but a mixture of the two forms melts at 163°.

Nitrosalicylonitrile and dinitrosalicylonitrile have been prepared by Victor Meyer and Bone. *Bromonitrosalicylonitrile*  $[\text{OH}:\text{CN}:\text{Br}:\text{NO}_2 = 1:2:4:6]$ , produced by the action of fuming nitric acid on bromosalicylonitrile, crystallises from petroleum in yellow needles, and melts at 119—120°. *Nitrosalicylonitrile*  $[\text{OH}:\text{CN}:\text{NO}_2 = 1:2:3]$  crystallises from boiling water in yellow leaflets, and melts at 207—208°.

The cryoscopic behaviour of the foregoing bromo- and nitro-compounds, and of the benzylic ether of salicylonitrile has been examined in naphthalene. The results are normal in the case of dibromocyanophenol, dinitrocyanophenol, and bromonitrocyanophenol, abnormal in the case of bromocyanophenol; nitrocyanophenol  $[\text{OH}:\text{CN}:\text{NO}_2 = 1:2:4]$  is sparingly soluble in naphthalene, whilst the isomeride,  $[\text{OH}:\text{CN}:\text{NO}_2 = 1:2:3]$ , is probably abnormal. M. O. F.

**Phenol-quinones and -quinhydrones.** Mixed Phenol-quinones. By ALFRED BILTRIS (*Chem. Centr.*, 1898, i, 887—888; from *Bull. Acad. roy. Belg.*, [iii], 35, 44—67).—When boiling solutions of absolutely pure paracresol (2 mols.) and quinone (1 mol.) in light petroleum are mixed, the liquid quickly becomes red, and *paracresol-quinone*,  $\text{C}_6\text{H}_4\text{O}_2, 2\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$ , soon crystallises out in red needles; it can be recrystallised from boiling ether, melts at 62°, sublimes without decomposing, and is soluble in ether, benzene, and hot light petroleum. *Orthocresol-quinone*, prepared in a similar way, crystallises in red needles and melts at 64°. Metacresol does not act on quinone. *Paracresol-phenol-quinone*,  $\text{C}_6\text{H}_4\text{O}_2, \text{PhOH}, \text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$ , obtained by mixing ethereal solutions of quinone, phenol, and cresol, and evaporating the ether, crystallises in reddish-brown needles, melts at 48°, decomposes spontaneously, and is soluble in benzene, ether, and hot light petroleum; *cresol-phenol-quinone* crystallises in reddish-brown needles and melts at 67°. *Thymol-phenol-quinone*,  $\text{C}_6\text{H}_4\text{O}_2, \text{PhOH}, \text{C}_6\text{H}_3\text{MePr}\cdot\text{OH}$ , prepared by mixing solutions of quinone, thymol, and phenol in ether and evaporating, crystallises in red needles, which, after about 2 days, change into small, blackish crystals; it melts at about 127°. When ethereal solutions of phenol (2 mols.) and toluquinone (1 mol.) are mixed and evaporated, *phenol-toluquinone*,  $\text{C}_6\text{H}_3\text{O}_2\text{Me}, 2\text{PhOH}$ , is obtained as a red syrup, which solidifies when immersed in a freezing mixture; it melts at 18°. *Phenol-thymoquinone*,  $\text{C}_6\text{H}_2\text{MePrO}_2, 2\text{PhOH}$ , prepared in like manner, is a red syrup which solidifies below 0°.

When lukewarm aqueous solutions of thymoquinol and ordinary quinone are mixed, thymoquinone instantly separates, and quinol with small quantities of the mixed quinhydrone remain in the mother liquor.

Determinations of the freezing points and boiling points of solutions of several quinhydrones and phenol-quinones show that both classes

of compounds are decomposed even in saturated solution in neutral solvents, and thus behave like additive compounds; this behaviour is also explained by Jackson and Oenslager's formula, in which a hemiacetal constitution is assumed.

E. W. W.

**Halogen Derivatives of Guaiacol and Veratrole.** By H. COUSIN (*Compt. rend.*, 1898, 127, 759—760).—*Trichloroguaiacol*, obtained by the action of chlorine on a chloroform solution of guaiacol, crystallises from alcohol in white needles and melts at 114—115°. The tetrachloro-derivative is not obtained by the prolonged action of chlorine. *Trichloroveratrole*, prepared by the action of methylic iodide on trichlorocatechol, or on the preceding compound, crystallises in white, prismatic needles and melts at 68—69°; it is somewhat insoluble in alcohol, but dissolves readily in benzene. *Dibromoguaiacol*, produced by direct bromination of guaiacol in cold chloroform solution, forms white, flattened, prismatic needles readily soluble in alcohol. *Tetrabromoguaiacol*, obtained by adding excess of bromine to guaiacol dissolved in concentrated sulphuric acid, crystallises from hot alcohol in clusters of prisms and melts at 160°. *Tribromoveratrole* results from the action of methylic iodide and alcoholic potash on tribromoguaiacol; it crystallises from alcohol in prismatic, silky needles, and melts at 83—84°.

G. T. M.

**Behaviour of Certain Groups of Cyclic Compounds towards Metallic Sodium.** By HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1898, 236, 542—570. Compare Abstr., 1898, i, 479).—The action of metallic sodium on chrysotropic acid in alcoholic solution has already been studied by the author, who now applies the reaction to a variety of substances, in order to find out how far the fluorescence, produced in some cases, is connected with the constitution of the compound. Among other conclusions, it is held that the reaction gives valuable information as to the constitution of certain tannin substances.

Phenol, thymol, anisol, phenetol, resorcinol dimethylic ether, anethoil, menthol, camphor, and caryophyllin, when treated with sodium in ethylic alcohol solution, do not give characteristic colour reactions. Catechol is turned green, then deep blue stripes appear on the glass, and a dark-green precipitate forms; resorcinol, blue-yellow to olive-green coloration; quinol, orange-yellow to brown coloration, and formation of an olive-green precipitate; orcinol, blood-red coloration, and flesh-coloured crusts form on the sodium, which, on standing, are changed into glistening, six-sided, rhombic prisms of the formula  $C_6H_3Me(ONa)_2 + H_2O$ . With pyrogallol, deep blue crusts are formed.  $\alpha$ -Naphthol gives a greenish-blue fluorescence;  $\beta$ -naphthol, a bluish-violet fluorescence, changing to olive, brown, and then orange; guaiacol, a yellow coloration, changing to green and then black; eugenol, an intense yellow coloration, and santonin an orange-red.

Salicylic acid gives a rose coloration changing to grey-green, with deposition of a grey, crystalline precipitate; protocatechuic acid, blue coloured crusts, dissolving in water to a yellowish-brown solution; gallic acid, blue crusts, or a blue solution changing to brownish-black, and formation of a colourless, crystalline precipitate, and tannin, bluish-green crusts, with production of a colourless, crystalline mass.

Orthomethoxycoumaraldehyde gives a yellow colour; cinnamic acid, microscopic, glistening needles of the composition  $\text{CHPhNa} \cdot \text{CHNa} \cdot \text{COONa}$ ; 3:4-dihydroxycinnamic acid, an intense dark-green coloration, and the yellow alcoholic solution of piperic acid is decolorised, and a white precipitate is formed.

From the behaviour of the various hydroxy-derivatives of coumarin, it appears that the fluorescence is intensified by the presence of side-chains in the benzene ring, but there is no direct relation between the intensity of the fluorescence and the number of entering hydroxy- or methoxy-groups. The author thinks it probable that fluorescence is due to the presence of the groups  $\text{OH}$  and  $\text{CH}:\text{CH} \cdot \text{COOH}$  in the ortho position, caused by the splitting of the lactone ring.

In order to study the influence exerted on the fluorescence by the removal of the carboxyl group, *orthovinylphenol*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CH}_2$ , was prepared by heating orthocoumaric acid; it is a yellow to greenish-brown oil, solidifying, on standing, to a brittle, glassy mass. Its alkaline solution is non-fluorescent, thus affording a definite proof of the fact that the fluorescence of orthocoumaric acid depends on the presence of the carboxyl group.

As the fluorescence of the above-mentioned substances is particularly noticeable in alkaline solution, the behaviour of organic bases was tried in this direction. A solution of chrysotropic acid (4-hydroxy-5-methoxycoumarol) in aniline is colourless, whilst in pyridine an intense yellow colour is produced. Both solutions are non-fluorescent. At the same time, beautifully crystalline, molecular compounds of the two substances are formed, and, as their solutions are highly refractive, the author proposes to prepare a number of these compounds, more particularly to study the influence of the various side-chains on the refractive properties of their solutions.

The sodium reaction has also been tried on the following tannin substances.

Glycosyl-dihydroxycinnamic acid gives an intense yellow coloration, and a golden-yellow precipitate of a sodium compound, dissolving in water to form a yellow solution, gradually changing to green and then brown; Fabianaglycotannin, from *Fabiana imbricata*, a similar behaviour to the above, but the colour of the aqueous solution of the sodium compound is a permanent yellow; Rochleder's boheic acid and tannin, from *Sorbus aucuparia*, intense yellow precipitates; maclurin, a yellow colour and precipitate; and catechin, a flesh-coloured precipitate changing to a brown resin.

Among the alkaloids, piperine gives an intense yellow colour, but no precipitate, when treated with sodium in alcoholic solution.

A. W. C.

**Formation of Chains. XXXI. Dimethylaniline and Etheral Salts of  $\alpha$ -Bromo-acids.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 3015—3025).—Weinig has stated (*Abstr.*, 1895, i, 17) that diethylaniline is a satisfactory agent for converting ethylic  $\alpha$ -bromisovalerate into ethylic dimethylacrylate, whilst dimethylaniline is unsuitable. The author finds that the latter base yields trimethylphenylammonium bromide with ethylic  $\alpha$ -bromopropionate, giving rise to unsaturated

salts with ethylic  $\alpha$ -bromisobutyrate and ethylic  $\alpha$ -bromisovalerate; ethylic  $\alpha$ -bromobutyrate, however, remains practically indifferent towards the base, illustrating the dissimilarity between the propionic and butyric radicles anticipated by the collision hypothesis.

[With TABASCHTSCHANSKY.]—*Trimethylphenylammonium bromide*,  $C_6H_4BrN$ , prepared from methylic bromide and dimethylaniline, is identical with the salt obtained from ethylic  $\alpha$ -bromopropionate and the base; it decomposes at  $203-204^\circ$ . Ethylic methylanilido-propionate,  $NMePh \cdot CHMe \cdot COOEt$ , the bye-product in the latter method of preparation, is identical with the salt obtained from ethylic bromopropionate and methylaniline (Abstr., 1898, i, 183); hydrolysis converts it into *methylyphenylalanine*,  $NMePh \cdot CHMe \cdot COOH$ , a viscous oil.

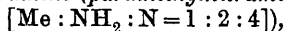
[With GRÜNBERG.]—Attempts to prepare ethylic methylanilido-butyrate (*loc. cit.*) from dimethylaniline and ethylic  $\alpha$ -bromobutyrate were unsuccessful.

[With BRODSKY.]—A polymeride of ethylic methylacrylate was obtained from dimethylaniline and ethylic  $\alpha$ -bromisobutyrate.

[With CARL BERNHARD.]—Ethylic dimethylacrylate was produced on heating ethylic  $\alpha$ -bromisovalerate with dimethylaniline during 6 hours; it is possible that a small quantity of ethylic  $\alpha$ -methylanilido-isovalerate was formed along with it. M. O. F.

**Formation of Chains. XXXII. Comparison of Aromatic Bases in their Behaviour towards Ethereal Salts of  $\alpha$ -Bromoacids.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 3025—3033).—A discussion and summary of the author's investigation of the influence exerted by the group  $\alpha$ ,  $\beta$ , X, Y, on the course of the change represented by the equation  $2NHXY + COOEt \cdot CabBr = NH_2XYBr + COOEt \cdot Cab \cdot NXY$ . M. O. F.

**Action of Ammonium Sulphide on Nitrated Aromatic Nitramines and Nitrosamines.** By JOHANNES PINNOW and PAUL R. OESTERREICH (*Ber.*, 1898, 31, 2926—2934. Compare Abstr., 1897, i, 338).—Paranitrophenylmethylnitramine is converted by ammonium sulphide in alcoholic solution into paranitromethylaniline, melting at  $152^\circ$ . Orthonitrophenylmethylnitramine may be prepared by the methylation of orthophenylnitramine, and is converted by alcoholic ammonium sulphide into orthonitromethylaniline melting at  $36^\circ$ . Orthonitroparatolylmethylnitramine is reduced by ammonium sulphide to *amidotolylmethylnitramine* (*paramethylnitramido-orthotoluidine*,



which crystallises in thin, dull red prisms melting at  $83.5^\circ$ . Paranitrophenylmethylnitrosamine is converted by ammonium sulphide into paranitromethylaniline, whilst orthonitroparatolylmethylnitrosamine yields the corresponding *amido*-compound (*methylnitrosamidotoluidine*), which crystallises in slender, sulphur-yellow needles melting at  $83^\circ$ . The *hydrochloride* is very unstable, but the *picrate* is more stable, and melts at  $103-105^\circ$ . This base readily undergoes the diazo-reaction, yielding a salt which reacts with  $\beta$ -naphthylamine to form *methylnitrosamido-orthotolueneazo- $\beta$ -naphthylamine*,  $C_{18}H_{17}N_5O$ ;

this crystallises in fiery red, slender needles melting at  $179^{\circ}$ . *Para-methylnitrosamido-orthoacetotoluidide*, prepared from the base by the action of acetic anhydride in ethereal solution, crystallises in yellowish prisms melting at  $142^{\circ}$ ; the *thiocarbamide* of the base melts at  $158^{\circ}$ .

*a*-Metaxylylidine is converted by methylic alcohol at  $170$ – $180^{\circ}$  into *methylxylidene*, which is an oil boiling at  $220.5$ – $221.5^{\circ}$ ; the corresponding *nitrosamine* is an uncrystallisable oil. *Acetomethylxylidene* crystallises in slender, white needles or compact prisms melting at  $65^{\circ}$ . Xylylmethylnitrosamine is converted by nitric acid into a *nitro*-compound which forms a heavy, almost white, crystalline powder melting at  $63^{\circ}$ , and has the constitution  $[\text{Me} : \text{N}_2 : \text{NO}_2 = 1 : 3 : 4 : 5]$ ; when heated with hydrochloric acid and aniline in alcoholic solution, it yields *nitromethylxylidene*, which melts at  $58^{\circ}$  and crystallises in long, carmine-red plates with a green reflex. This compound, by reduction with tin and hydrochloric acid, is converted into *methylxylidene-diamine*,  $\text{C}_9\text{H}_{14}\text{N}_2$ , which boils at  $260$ – $262^{\circ}$  and yields a crystalline *hydrochloride* melting at  $225^{\circ}$ . Nitrous acid converts this substance almost quantitatively into *methylazimidoxylene*,  $\text{C}_9\text{H}_{11}\text{N}_3$ , which crystallises in nodular aggregates of almost colourless needles melting at  $118.5$ – $119^{\circ}$ ; this reaction shows that the two amido-groups are in the ortho-position. *Diacetylmethylxylidenediamine* crystallises in broad needles melting at  $195$ – $196^{\circ}$ . Nitroxylylmethylnitrosamine is reduced by ammonium sulphide to *amidoxylylmethylnitrosamine*, which crystallises in lustrous plates melting at  $81^{\circ}$ ; the *picrate* melts at  $128^{\circ}$ . *Methylnitrosamido-symmetrical-xyleneazo- $\beta$ -naphthylamine*, prepared in the usual manner, crystallises in long, lustrous, red plates melting at  $184^{\circ}$ . *Acetamidoxylylmethylnitrosamine* crystallises in thin, white plates melting at  $135^{\circ}$ . *Methylnitrosamido-xylylphenyl-thiocarbamide* forms thick prisms and melts at  $132$ – $132.5^{\circ}$ .

A. H.

**Nitrations with Nitrous Acid.** By JOHANNES PINNOW (*Ber.*, 1898, 31, 2982–2987).—It has been shown in several cases (*Abstr.*, 1898, i, 134, &c.) that when a para-substituted dialkylaniline is nitrated by means of nitrous acid, the nitro-group takes the ortho-position relatively to the alkylamido-group. The formation of the substance described by Koch (*Abstr.*, 1887, 1041) as metanitropara-chlorodimethylaniline appeared, therefore, anomalous; it is shown, however, that this substance is really an ortho-compound  $[\text{NMe}_2 : \text{NO}_2 : \text{Cl} = 1 : 2 : 4]$ , for when it is reduced with tin and hydrochloric acid and the product fractionated, a base is obtained (4-chloro-2-amidodimethylaniline; boils at  $266.5$ – $267.5^{\circ}$  under a pressure of 751 mm.; the yellow *picrate* melts at  $190$ – $191^{\circ}$ ), which, when heated with acetic anhydride at  $145$ – $160^{\circ}$ , yields *N- $\alpha$ -dimethyl-2-chlorobenzimidazole*,  $\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NMe} \end{smallmatrix} \text{CMe}$ , melting at  $130$ – $131^{\circ}$ , whilst its *mercurochloride* melts at  $277$ – $278^{\circ}$ ; moreover, the higher boiling fraction obtained in the reduction yields the *mercurochloride*, melting at  $243$ – $244^{\circ}$ , of *N-methyl-2-chlorobenzimidazole*,  $2\text{C}_6\text{H}_3\text{Cl} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NMe} \end{smallmatrix} \text{CH}, \text{H}_2\text{HgCl}$  (compare *Abstr.*, 1898, i, 182).

When 4-chlorodimethylaniline is dissolved in dilute sulphuric acid and nitrated with dilute nitric acid, the product is a yellowish-red 4-chlorodinitrodimethylaniline  $[(\text{NO}_2)_2 = 2:6 \text{ (?)}]$ , which melts at 111—112°. When it is nitrated at  $-10^\circ$  with strong sulphuric acid and nitric acid of sp. gr. = 1.4, 4-chloro-3-nitrodimethylaniline is the product; this is yellow, and melts at 81.5—82.5°.

It would seem that nitrous acid is incapable of effecting nitration when the ortho-position relatively to the dimethylamido-group is already occupied.

C. F. B.

Derivatives obtained by the Action of Carbon Bisulphide on Dimethylaniline. By JOH. WEINMANN (*Chem. Centr.*, 1898, i, 1028—1029; from *Bull. Soc. ind. Mulhouse*, 1898, 40—43).—Carbon bisulphide alone does not act on dimethylaniline even at high temperatures, but in presence of metallic salts, such as zinc chloride, the following compounds are obtained. Dimethylamidothiobenzoic acid is prepared by shaking a mixture of 4 kilograms of carbon bisulphide, 30—40 kilograms of dimethylaniline, and 20 kilograms of zinc chloride for about 100 hours at 60—70°. The zinc chloride is removed by shaking with water containing acetic acid, the thio-acid being extracted with sodium hydroxide solution and precipitated with hydrochloric acid. Tetramethyldiamidodiphenyl thioketone is prepared by keeping the above mixture at 80° for 100—120 hours, removing the unchanged thio-acid, filtering off the zinc sulphide, removing the excess of dimethylaniline by distillation with steam, and finally treating the residual thioketone with very dilute hydrochloric acid to remove hexamethylparaleucaniline. The thioketone crystallises from carbon bisulphide in large crystals with a lustre like that of iodine, and, when heated with alcoholic ammonia under pressure, yields auramine, whilst with alcoholic aqueous ammonia it forms Michler's ketone. Hexamethylparaleucaniline is obtained by heating the mixture of carbon bisulphide, dimethylaniline, and zinc chloride at 100°. Tetramethylthioaniline is prepared by keeping the above mixture for several hours at 130—140°. After removing the thio-acid and dimethylaniline, the thio-base is separated from the diphenylmethane base,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , which is also formed by fractional crystallisation from alcohol, or by precipitating the solution of the hydrochloride with excess of hydrochloric acid. Tetramethylthioaniline crystallises in lemon-coloured prisms, and melts at 178° (uncorr.); the hydrochloride, which forms colourless leaflets, gradually becoming yellow when exposed to the air, is decomposed by water. The sulphur is possibly in the para-position relatively to the dimethylamido-group, for in Tursini's isomeric base which melts at 125°, these groups occupy relatively the ortho-position.

E. W. W.

Tertiary Aromatic Amines. I. By CARL HAEUSSERMANN and EUGEN BAUER (*Ber.*, 1898, 31, 2987—2989).—Triphenylamine, when treated in acetic acid solution at the ordinary temperature with sodium nitrite, yields nitrotriphenylamine (Herz, *Abstr.*, 1890, 1409).

Diphenylorthotoluidine,  $\text{NPh}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , was obtained by dissolving potassium (1 part) in diphenylamine (15 parts), heating the solution to 240—245°, and adding orthochlorotoluene (3.5 parts) gradually;

after 2—3 hours the product was allowed to cool and extracted with ether; from the extract, the ether was first distilled off, and then the excess of chlorobenzene and diphenylamine under reduced pressure; the residue was dissolved in light petroleum, any diphenylamine still present was precipitated as the hydrochloride by passing in gaseous hydrogen chloride, and the residue was freed from hydrogen chloride and petroleum, and then distilled under a pressure of 60 mm., when the fraction that boiled above  $275^{\circ}$  was found to solidify in part after several months; the crystals melted at  $69-70^{\circ}$ . When diphenylorthotoluidine is dissolved in acetic acid and treated with sodium nitrite, a yellow *mononitro*-derivative, melting at  $164-165^{\circ}$ , is obtained; if nitric acid is added instead of sodium nitrite, no such derivative is formed. C. F. B.

**Combination of Phenylhydrazine with Metallic Salts.** By PASTUREAU (*Compt. rend.*, 1898, 127, 485—486).—When 5 grams of melted phenylhydrazine is added gradually to a boiling solution of 10 grams of bismuth chloride in 100 c.c. of dilute hydrochloric acid, and the liquid is evaporated at a gentle heat to about one-third of its bulk and allowed to cool, the compound  $\text{BiCl}_3 \cdot 6\text{N}_2\text{H}_3\text{Ph}$  separates in masses of colourless needles; it dissolves in dilute acids, and the solutions give all the reactions of the bismuth salt and phenylhydrazine.

The compound  $\text{Bi}_3\text{NO}_3 \cdot 6\text{N}_2\text{H}_3\text{Ph}$  is obtained in colourless, prismatic needles in a similar manner, but the temperature must not at any stage exceed  $60^{\circ}$ , or oxidation will take place. Its solution likewise gives all the reactions of the bismuth salt and phenylhydrazine.

The compound  $\text{ZnSO}_4 \cdot 2\text{N}_2\text{H}_3\text{Ph}$  is obtained in colourless needles by dissolving 10 grams of zinc chloride in 100 c.c. of dilute acid, adding 50 c.c. of the ordinary solution of sodium hydrogen sulphite, and 5 grams of phenylhydrazine. A manganese compound,  $\text{MnSO}_4 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ , is obtained in a similar way. C. H. B.

**Compounds of Phenylhydrazine with Haloid Salts of the Alkaline Earth Metals.** By JOSEPH MOITTESSIER (*Compt. rend.*, 1898, 127, 722—723).—The compound  $\text{CaCl}_2 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ , obtained by adding phenylhydrazine to an alcoholic solution of calcium chloride, crystallises from hot alcohol in rhombic plates and readily dissolves in water, but is insoluble in ether. The strontium compound is unstable. The compound  $\text{CaBr}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph} + 3\text{H}_2\text{O}$ , which crystallises in long needles when phenylhydrazine is added to an aqueous solution of calcium bromide, is soluble in alcohol, but not in ether; when boiled with benzene, the whole of the aromatic base is eliminated. The compound  $\text{SrI}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$  is obtained in prismatic crystals from an alcoholic solution of its components; it is deliquescent and decomposes at  $100^{\circ}$ . The corresponding compound from strontium bromide is also deliquescent; it is decomposed by dry ether. Phenylhydrazine combines with the fluorides of the zinc group, but not with those of calcium or strontium; it forms analogous compounds with lithium bromide and with the benzoates and oxalates of the zinc group. G. T. M.

**Action of Phenylhydrazine on Chloranilic Acid.** By A. DESCOMPS (*Compt. rend.*, 1898, 127, 665—666).—On adding chloranilic

acid (1 mol.) dissolved in alcohol, drop by drop, to an alcoholic solution of phenylhydrazine (3 mols.), the compound  $C_6Cl_2O_2(OH)_2, 2N_2H_3Ph$  separates on standing in slender, brownish-violet crystals; this action corresponds with that of phenylhydrazine on phloroglucinol (Baeyer and Kochendoerfer, *Abstr.*, 1889, 1162), and on quinol and orcinol (Seyewitz, *Abstr.*, 1892, 49).

W. A. D.

**Isomeric Benzoylacetoximes.** By JULIUS SCHMIDT (*Ber.*, 1898, 31, 3225—3229).—When sodium wire (4.6 grams) is gradually covered with a solution of acetoxime (14.6 grams) in perfectly dry ether, the reaction is at first violent, but slackens and requires some four days before it is completed; the sodium salt is well washed with dry ether, then suspended in ether, and treated with rather less than the theoretical quantity of benzoic chloride. The oil which is left after distilling off the ether partially solidifies, and is a mixture of a liquid benzoylacetoxime with the solid one already described by Janny (*Abstr.*, 1883, 581); these may be separated by the aid of a suction pump. Janny's compound,  $CMe_2 \cdot N \cdot O \cdot CPh$ , is readily soluble in alcohol, ether, chloroform, or benzene, sparingly in light petroleum, melts at  $43-44^\circ$  (Janny gives  $41-42^\circ$ ), and is slowly hydrolysed by dilute sodium hydroxide, but is not acted on by 1 per cent. solution of sodium carbonate; it is soluble in cold fuming hydrochloric acid, but after a few hours benzoic acid is deposited, and under certain circumstances a compound melting at  $30-32^\circ$ , and probably a benzoylhydroxylamine,

is formed. The liquid isomeride,  $C \begin{smallmatrix} N \cdot CPh \\ \diagup \\ CMe_2 \end{smallmatrix}$ , is a pale yellow, mobile,

oil of sp. gr. = 1.0981 at  $14/4^\circ$  and refractive index  $n_D = 1.5279$  at  $14^\circ$ , miscible in all proportions with alcohol, ether, chloroform, or benzene. One hundred parts of light petroleum (b. p.  $50-60^\circ$ ) dissolve, at  $20^\circ$ , 6.58 parts of the oil. Its alcoholic solution, when treated with ferric chloride, gives an intense red-violet coloration. It is slowly transformed at the atmospheric temperature into Janny's compound, more quickly when treated with alkalis.

J. J. S.

**Benzoate of Acetohydroxamic Acid.** By FRANK K. CAMERON (*J. Physical Chem.*, 1898, 2, 376—381).—The benzoate of acetohydroxamic acid (Jones, *Abstr.*, 1898, i, 172) has a melting point of  $99^\circ$ , but on precipitating the compound from its solution in ether by the addition of light petroleum, an isomeric modification melting at  $70^\circ$  is obtained. The author calls the first the  $\alpha$ -, and the second the  $\beta$ -compound. Both modifications exist in the liquid phase. The  $\alpha$ -modification is the stable one at the ordinary temperature. Crystals of the  $\beta$ -modification can be obtained by dissolving the  $\alpha$ -compound and precipitating suddenly from solution; the  $\alpha$ -modification is converted into the  $\beta$ -modification with absorption of heat. By raising the temperature of the system and cooling rapidly, the point of solidification may be brought below the stable triple point. It is not possible to realise the eutectic point in this manner, as the compound decomposes; the eutectic point is near  $65^\circ$ . The temperature of the stable triple point is about  $95^\circ$ .

H. C.



**Modification of Friedel and Craft's Method of Synthesis by aid of Aluminium Chloride.** By A. VERLEY (*Bull. Soc. Chim.*, 1897, [iii], 17, 906—914).—In order to eliminate the hydrogen chloride formed in the action and to prevent the formation of resinous substances, the author carries out the condensation at 0° and in a vacuum, the acid or alkyl chloride being added drop by drop to a cooled mixture of the hydrocarbon with aluminium chloride; the yield is good, and the method is especially advantageous in the preparation of ketones. Thus, by the action of acetic chloride on the corresponding hydrocarbons, the author has obtained yields of 80 per cent. of paratolyl methyl ketone, metaxylyl methyl ketone [Me : Me : Ac = 1 : 3 : 4], and paracymyl methyl ketone [Me : Ac : Pr<sup>β</sup> = 1 : 2 : 4]; he contradicts the statement of Essner and Gossin (*Abstr.*, 1885, 252), that metatolyl methyl ketone is produced by this method. *Paratolyl bromomethyl ketone*, melting at 51°, and *paratolyl dibromomethyl ketone*, melting at 99°, are produced by the action of one and of two molecules of bromine on paratolyl methyl ketone; the monobromo-derivative is readily oxidised by alkaline potassium permanganate to paratolylglyoxylic acid, C<sub>6</sub>H<sub>4</sub>Me·CO·COOH, which, when heated with aniline, loses carbonic anhydride and gives the corresponding aldehyde. This is a general method for preparing aromatic aldehydes, and from cymene the author has thus obtained *methylisopropylbenzaldehyde*, [Me : CHO : Pr<sup>β</sup> = 1 : 2 : 4]; this boils at 132° under a pressure of 20 mm., or at 238° under 760 mm. pressure; and has a sp. gr. = 0.9988 at 0°. It has an unpleasant odour recalling that of carrots, and in presence of a trace of sodium condenses with acetone to form the compound C<sub>3</sub>H<sub>7</sub>·C<sub>6</sub>H<sub>3</sub>Me·CH·CH·CO·CH<sub>3</sub>, which has the characteristic odour of saffron.

The first product of the action of ethylic chloroglyoxylate on paracymene is *ethylic cymylglyoxalate*,

C<sub>6</sub>H<sub>3</sub>MePr<sup>β</sup>·CO·COOEt [Me : C<sub>2</sub>O<sub>3</sub>Et : Pr<sup>β</sup> = 1 : 2 : 4], of which, however, only a 20 per cent. yield could be obtained; this boils at 130—132° under a pressure of 21 mm., or under atmospheric pressure at 237° with decomposition; its sp. gr. = 0.9841; it has a disagreeable odour, which, when diluted, is somewhat suggestive of violets; by the further action of aluminium chloride, it loses carbonic oxide and anhydride, and is converted into ethylcymene [Me : Et : Pr<sup>β</sup> = 1 : 2 : 4]. When chloromethylic ethylic ether is added to a mixture of benzene and aluminium chloride, it gives a theoretical yield of diphenylmethane, and can, therefore, be used with advantage in place of methylenic chloride for the preparation of this substance; the first product of the action is probably benzylic ethylic ether, which, in presence of hydrogen chloride, is converted into benzylic chloride, and then condenses with a second molecule of benzene. T. M. L.

**Chlorophosphine of Orthochlorotoluene.** By P. MELCHIKER (*Ber.*, 1898, 31, 2915—2919).—2-Chlorotolyl-4-chlorophosphine, C<sub>6</sub>H<sub>3</sub>MeCl·PCl<sub>2</sub>, can be obtained from 2-chlorotoluene (compare *Abstr.*, 1897, i, 146), but the yield is small; it boils at 265—266°, and has a sp. gr. = 1.373 at 22°. When decomposed with water, it forms the

*phosphinous acid*,  $C_6H_3MeCl \cdot P(OH)_2$ ; this melts at  $70^\circ$ ; its yellow *phenylhydrazine* salt at  $156.5^\circ$ ; the anhydrous *ammonium* and *barium* salts were also analysed. The *tetrachloride*,  $C_6H_3MeCl \cdot PCl_4$ , crystallises in pale yellow needles; when treated with sulphurous anhydride, it yields the *oxychloride*,  $C_6H_3MeCl \cdot POCl_2$ , which melts at  $36^\circ$  and boils at  $290-291^\circ$ . When this is warmed with water, it is converted into *2-chlorotolyl-4-phosphinic acid*,  $C_6H_3MeCl \cdot PO(OH)_2$ , which melts at  $190^\circ$ ; the normal *silver*, and the *silver*, *barium*, and *aniline hydrogen* salts of this acid, all of them anhydrous, were analysed; when the acid is heated with bromine and water, it is converted into phosphoric acid and *2-chloro-4-bromotoluene* (Willgerodt and Salzmann, Abstr., 1889, 985); when it is dissolved in fuming nitric acid, and the solution is diluted with water, the product is a yellowish *mononitro*-derivative, melting at  $200^\circ$  and exploding at a higher temperature, of which the yellow *barium hydrogen* and normal *lead* and *silver* salts were analysed; when it is oxidised with alkaline permanganate at  $50-60^\circ$ , it yields *2-chlorobenzo-4-phosphinic acid*,  $COOH \cdot C_6H_3Cl \cdot PO(OH)_2$ , melting at  $254^\circ$ , of which the *barium hydrogen* salt was analysed.

C. F. B.

$\alpha$ - and  $\beta$ -Trimethylphosphortolubetaines, and their Carboxylic Acids. By FR. CONEN (*Ber.*, 1898, 31, 2919-2924).—1:3-Xylylchlorophosphine,  $C_6H_3Me_2 \cdot PCl_2$  (Weller, Abstr., 1887, 824), which consists of a mixture of two isomerides [ $PCl_2 = 4$ , ( $\alpha$ ); and probably 5, ( $\beta$ )], was converted by treatment with pure zinc methyl into *dimethylxylylphosphine*,  $C_6H_3Me_2 \cdot PMe_2$ , which boils at  $233^\circ$  (a little *dimethylxylylphosphine oxide*,  $C_6H_3Me_2 \cdot PMe_2O$ , was also obtained as a syrup; the crystalline *mercurichloride* of this,

$C_6H_3Me_2 \cdot PMe_2(OH)_2 + HgCl_2$ , was analysed); from this phosphine, the phosphonium iodide,  $C_6H_3Me_2 \cdot PMe_3I$ , was prepared by treatment with methylic iodide in ethereal solution. By fractional crystallisation, this iodide was separated into two isomerides; the less soluble melts at  $265^\circ$ , and was identified as 1:3-xylyl-4-phosphonium iodide ( $\alpha$ ) since it could also be prepared from 1:3:4-mercurydixylyl. From it, a crystalline, hygroscopic, alkaline hydroxide was prepared by treatment with moist silver oxide, and from this the hygroscopic *chloride*,  $C_6H_3Me_2 \cdot PMe_3Cl$ , melting at  $110^\circ$ . When oxidised with the theoretical quantity of potassium permanganate at  $55^\circ$ , this chloride yields the deliquescent *betaine chloride*,  $COOH \cdot C_6H_3Me \cdot PMe_3Cl$ , of which the orange-yellow *platinochloride* was analysed; by treating the betaine chloride with

sodium carbonate,  $\alpha$ -trimethylphosphortolubetaine,  $C_6H_3Me \begin{smallmatrix} \text{CO} \\ \diagup \text{PMe}_3 \diagdown \end{smallmatrix} O$ , was obtained; this is very hygroscopic; the *nitrate* and golden-yellow *picrate* melt at  $226^\circ$  and  $220^\circ$  respectively. When the phosphonium chloride is oxidised at  $60-70^\circ$  with the amount of permanganate necessary to convert both methyl groups into carboxyl, the crystalline *chloride*,  $PMe_3Cl \cdot C_6H_3(COOH)_2$ , is obtained (the *platinochloride* melts at  $258^\circ$ ); by treating this with the calculated quantity of moist silver oxide,  $\alpha$ -trimethylphosphortolubetainecarboxylic acid,

$\text{COOH} \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{CO} \\ \text{PMe}_3 \end{smallmatrix} \right\rangle \text{O}$ , is formed; this melts at  $160^\circ$ ; its blue *copper* salt,  $\text{OH} \cdot \text{PMe}_3 \cdot \text{C}_6\text{H}_3 : [\text{COO}] :_2 \text{Cu}$ , was analysed.

The more soluble of the two phosphonium iodides mentioned above melts at  $205^\circ$ ; it is the  $\beta$ - (probably 1:3:5) compound. A series of analogous derivatives was prepared from it; of these, the *betaine-carboxylic acid* melts at  $115^\circ$ .  
C. F. B.

**Primary Chlorostibines of the Aromatic Series.** By J. HASENBÄUMER (*Ber.*, 1898, 31, 2910—2914. Compare Michaelis and Reese, *Abstr.*, 1886, 885).—When mercury diphenyl and antimony trichloride are heated together at  $130^\circ$  in xylene solution, triphenylstibine chloride,  $\text{SbPh}_3\text{Cl}_2$ , and some diphenylstibine chloride,  $\text{SbPh}_2\text{Cl}_3 + \text{H}_2\text{O}$ , are formed. By heating triphenylstibine with antimony chloride and a little xylene at  $240^\circ$  for 48 hours continuously, *phenylchlorostibine*,  $\text{SbPhCl}_2$ , can be obtained, which melts at  $58^\circ$  and boils at  $290^\circ$ , and emits a very unpleasant odour when heated; aqueous sodium carbonate converts it into *phenylstibine oxide*,  $\text{SbPhO}$ , which melts at  $150^\circ$ , whilst with alcoholic ammonium sulphide, it yields *phenylstibine sulphide*,  $\text{SbPhS}$ , which melts at  $65^\circ$ . When it is saturated with gaseous hydrogen chloride in ethereal solution, crystalline, hygroscopic *phenyltetrachlorostibine* is obtained, and when this is dissolved in caustic soda, *phenylstibic acid*,  $\text{SbPhO}(\text{OH})_2$ , is formed; this is an amorphous powder which decomposes above  $200^\circ$ , and dissolves in alkali carbonates and ammonia as well as in caustic alkalis; its anhydrous *barium hydrogen salt*, which forms a white precipitate, was analysed.

*Paratolylchlorostibine*, which was prepared in a similar manner, melts at  $93.5^\circ$ , boils above  $360^\circ$ , and yields a series of analogous derivatives; of these, the *oxide* melts at  $200^\circ$ .  
C. F. B.

**Phenoxyacetic Acid. Phenylic Phenoxyacetate and its Bromo-derivatives.** By ALB. J. J. VANDEVELDE (*Chem. Centr.*, 1898, i, 988—989; from *Bull. Acad. roy. Belg.*, [iii], 35, 223—237).—*Phenoxyacetic chloride*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{COCl}$ , is prepared by warming a mixture of 100 grams of phenoxyacetic acid with 145 grams of phosphorus pentachloride, the fraction which boils at  $160$ — $170^\circ$  under 60 mm. pressure being rectified at the ordinary pressure. It is a colourless, fuming liquid, boils at  $225$ — $226^\circ$ , and acts on water with violence. *Phenylic phenoxyacetate*,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{COOPh}$ , is obtained by the action of phenoxyacetic chloride on phenol. The product after being washed with sodium hydroxide solution and water and distilled, yields a fraction which boils at  $236^\circ$  under 73 mm., or at  $320$ — $325^\circ$  under the ordinary pressure, and solidifies to a butyraceous mass; it can be crystallised from chloroform, and is soluble in the ordinary organic solvents. It is not attacked by sodium carbonate in the cold, but is hydrolysed on heating. With phenylhydrazine in alcoholic solution, it forms crystals of *phenoxyacetophenylhydrazide*, which melts at  $180^\circ$ . By the action of bromine (1 mol.) dissolved in carbon bisulphide, carbon tetrachloride or chloroform on phenylic phenoxyacetate (1 mol.), *phenylic parabromophenoxyacetate*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOPh}$ , is formed; it crystallises from ether, melts at  $73^\circ$ , is insoluble in water, soluble in the ordinary organic

solvents, and is hydrolysed by boiling sodium carbonate solution. With an alcoholic solution of phenylhydrazine, it yields *parabromophenoxyacetylphenylhydrazide*,  $C_6H_4Br \cdot O \cdot CH_2 \cdot CO \cdot N_2H_3Ph$ , which separates from boiling alcohol in white crystals and melts at  $174^\circ$ .

*Parabromophenylic phenoxyacetate*,  $OPh \cdot CH_2 \cdot COO \cdot C_6H_4Br$ , obtained by the action of parabromophenol on phenoxyacetic chloride, separates from chloroform in colourless crystals, melts at  $98^\circ$ , and is soluble in the ordinary organic solvents, but insoluble in water. It is hydrolysed by hot sodium carbonate solution, and with phenylhydrazine yields the same compound as phenylic phenoxyacetate. *Parabromophenoxyacetic chloride*,  $C_6H_4Br \cdot O \cdot CH_2 \cdot COCl$ , prepared by the action of phosphorus pentachloride on bromophenoxyacetic acid, boils at  $259^\circ$ , reacts violently with water, and when cooled forms a butyraceous mass which melts at  $42^\circ$ ; with phenol, in presence of phosphorus oxychloride, which prevents the formation of resinous substances, it yields phenylic parabromophenoxyacetate.

E. W. W.

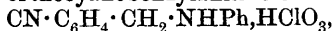
**Derivatives of Orthotoluenitrile.** By WILLY LANDSBERGER (*Ber.*, 1898, 31, 2880—2889).—*Paranitro-orthotoluenitrile*,

$CN \cdot C_6H_3Me \cdot NO_2$  [ $Me : CN : NO_2 = 1 : 2 : 4$ ], obtained when the orthonitrile (6 grams) is gradually added to well-cooled fuming nitric acid (30 c.c.), and the resulting yellow solution poured on to ice, crystallises from boiling alcohol in needles, melts at  $105^\circ$ , sublimes at  $100^\circ$  in long, slender needles, is readily soluble in acetone, chloroform, ethylic acetate, benzene, and hot alcohol, sparingly in ether, carbon bisulphide, acetic acid or hot water, and almost insoluble in light petroleum. When warmed for about  $1\frac{1}{2}$  hours with 10 times its weight of concentrated sulphuric acid, it yields *nitrotoluenamide*, which crystallises from boiling water in glistening needles, melts at  $173^\circ$ , and is only sparingly soluble in ether or light petroleum. When hydrolysed with fuming hydrochloric acid, it yields 4-nitro-orthotoluic acid. *4-Amido-orthotoluenitrile*, is obtained when an alcoholic solution of the nitro-derivative is reduced with tin and hydrochloric acid until a portion of the solution yields no oil on pouring into water. The base crystallises from boiling light petroleum in colourless, felted needles melting at  $88^\circ$ , and readily turning brown on exposure to the air. The *hydrochloride*,  $C_8H_8N_2 \cdot HCl$ , crystallises from absolute alcohol in yellowish, glistening needles melting at about  $220^\circ$ ; the *picrate* crystallises in lemon-yellow needles and melts at  $177$ — $179^\circ$ , and the *platinochloride* decomposes slowly above  $240^\circ$ .

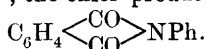
*Orthocyanobenzylaniline*,  $CN \cdot C_6H_4 \cdot CH_2 \cdot NHPh$ , is obtained when orthocyanobenzyl chloride (6 grams) is added to aniline (14 c.c.) heated to  $90^\circ$ , and the mixture kept at that temperature for an hour; it is then rendered alkaline, the excess of aniline distilled in steam, and the product precipitated with potassium hydroxide and recrystallised from alcohol; it melts at  $124$ — $126^\circ$ , and is insoluble in water, but readily dissolves in benzene, acetone, or alcohol. The *hydrochloride* turns grey at  $120^\circ$ , and completely decomposes at  $238^\circ$ . The *picrate* crystallises in yellow needles melting at  $186^\circ$ , and the *platinochloride* decomposes at about  $223^\circ$ .

Attempts have been made to prepare orthocyanobenzaldehyde by

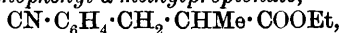
Berg's method (Abstr., 1898, i, 553), but on warming a solution of orthocyanobenzylaniline hydrochloride with excess of sodium hypochlorite, crystals of orthocyanobenzylaniline chlorate,



are obtained, they melt at  $171^\circ$ , again solidify, and on further heating decompose. When orthocyanobenzylaniline is oxidised with potassium permanganate at  $15-20^\circ$ , the chief product is phthalanil,



*Ethylic  $\beta$ -orthocyanophenyl- $\alpha$ -methylpropionate,*



is obtained when ethylic methylacetoacetate (4.8 grams) is added to a 2N-alcoholic sodium solution (17 c.c.) and then, to this, a solution of orthocyanobenzyl chloride (5 grams) in absolute alcohol (20 c.c.); after 90 hours, only some 75 per cent. of the alkali is used up. The ethereal salt, which is isolated by distillation, passes over last of all; it boils at about  $270^\circ$ , and is practically insoluble in concentrated hydrochloric acid. It is hydrolysed when heated with concentrated hydrochloric acid for 2 hours at  $100^\circ$ , and the  *$\beta$ -orthocyanophenyl- $\alpha$ -methylpropionic acid* formed crystallises from boiling water in colourless needles melting at  $99^\circ$ ; it is readily soluble in most solvents with the exception of carbon bisulphide.  *$\beta$ -Orthocarboxyphenyl- $\alpha$ -methylpropionic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{COOH}$ , formed when the ethylic salt is hydrolysed with concentrated hydrochloric acid at  $160^\circ$ , crystallises from hot water in colourless prisms melting at  $142^\circ$ . Its *silver* salt crystallises in minute needles. All attempts to obtain hydrindone derivatives from it have proved fruitless.

*$\beta$ -Orthocyanophenyl- $\alpha$ -ethylpropionic acid*, crystallises from boiling water in glistening plates melting at  $67-68^\circ$ ; and its *silver* salt melts at  $180^\circ$ .  *$\beta$ -Orthocarboxyphenyl- $\alpha$ -ethylpropionic acid* is readily soluble in most organic solvents, and crystallises from hot water in long, colourless, glistening needles melting at  $140-141.5^\circ$ . J. J. S.

**Ethylic  $\alpha$ -Phenylacetoacetate.** By WALTER BECKH (*Ber.*, 1898, 31, 3160—3164.)—Ethylic  $\alpha$ -phenylacetoacetate cannot be obtained in any quantity by the action of ethylic acetate on ethylic phenylacetoacetate in presence of sodium ethoxide, the chief products of the reaction being ethylic acetoacetate and ethylic diphenylacetoacetate. It can, however, be obtained from *aceto-benzyl cyanide*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CN}$ , which is formed by the action of ethylic acetate on benzyl cyanide in presence of sodium ethoxide, and is a dazzling white, crystalline mass melting at  $90^\circ$ . When this compound, in solution in absolute ethylic alcohol, is treated with hydrogen chloride, the free hydrogen chloride then removed by exposing the solution over solid potash, and the residue warmed with the calculated amount of water, *ethylic  $\alpha$ -phenylacetoacetate*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CHPh} \cdot \text{COOEt}$ , is produced, a yield of about 55 per cent. of the theoretical being obtained. It is a colourless oil which boils at  $145-147^\circ$  under a pressure of 11 mm., and readily undergoes the characteristic hydrolysis of the ethereal salts of the ketonic acids,

yielding phenylacetic acid or benzyl methyl ketone, according to the hydrolytic agent employed.

*Ethylc sodiophenylacetate* is an extremely hygroscopic powder; the *phenylhydrazone* crystallises in white needles melting at  $104^{\circ}$ , and is readily converted by boiling glacial acetic acid into 1:4-diphenyl-3-methyl-5-pyrazolone,  $\text{CMe} \begin{array}{c} \text{N} \text{---} \text{NPh} \\ \diagup \quad \diagdown \\ \text{CHPh} \cdot \text{CO} \end{array}$ , which crystallises in white needles melting at  $196^{\circ}$ .

A. H.

**Supposed Identity of Tannin and Digallic Acid.** By PAUL WALDEN (*Ber.*, 1899, 31, 3167—3174).— $\alpha$ -Digallic acid, prepared according to Schiff's directions, by the action of arsenic acid on gallic acid dissolved in alcohol, has no definite melting point, but sinters at  $120^{\circ}$  and begins to decompose at  $150^{\circ}$ ; it dissolves readily in acetone, ethylic acetate, ethylic and amylic alcohols, and in acetic acid. Its molecular weight in boiling acetone is about 316, whilst the molecular weight of tannin, obtained from Schuchardt, was 1350—1560, that of another sample, obtained from Merck, being about 753—763, that is to say, 2 to 4 times as great as that of digallic acid (compare Paternò, *Abstr.*, 1890, 105, and Sabanéeff, *Abstr.*, 1891, 145).

The affinity coefficient of  $\alpha$ -digallic acid is  $K=0.0012$ ; that of tannin varies greatly with the concentration, and is very much smaller than the above number.

When tannic acid, dissolved in dilute alcohol, is titrated with N/20 baryta water in presence of phenolphthalein, a cloudy, blood-red liquid is formed, whilst digallic acid, under similar circumstances, gives a clear, reddish liquid; in neither case is the end reaction definite.

Spectrometric examination of solutions of tannin and digallic acid shows that their absorptive powers for all regions of the spectrum are entirely different, the extinction coefficient of tannin being always considerably lower than that of digallic acid. When a 10 per cent. solution of tannin is mixed with a 5 per cent. alcoholic solution of arsenic acid, the whole liquid sets to a transparent, glass-like mass, which does not liquefy when warmed, but darkens when strongly heated, and, when dried, is insoluble in most of the usual media, but dissolves in soda and is reprecipitated on addition of mineral acids; the addition of arsenic acid also causes a speedy reduction of the rotatory power of the solution. If a solution of digallic acid be treated in a similar manner, it remains liquid for months.

The above facts, as well as those observed by other workers in this field, make it clear that there is no longer any reason whatever to suppose that tannin and digallic acid are identical.

A. L.

**Sacchareins. A New Class of Colouring Matters Derived from Orthobenzoic Sulphinide.** By PAUL MONNET and J. KÖTSCHET (*Bull. Soc. Chim.*, 1897, 17, [iii], 690—702).—Orthobenzoic sulphinide ("saccharin") condenses with phenols, forming products whose constitutions are of a type similar to that of the phthaleins. Thus, with phenol, the product has the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2 \\ \text{SO}_2 \end{array} \text{NH}$ ,

and dissolves in alkali, giving a red solution which is decolorised on the addition of acids.

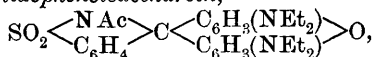
Resorcinol and orthobenzoic sulphinide interact at 200—220° in presence of aluminium chloride; the crude product, after treatment with dilute aqueous sodium carbonate, is a brownish-red mass whose solution in hot dilute alkalis has a marked orange-yellow colour, and, on dilution, exhibits a powerful green fluorescence. The colouring matter is precipitated by acids, and can be purified by dissolving it in alcohol and reprecipitating with water; it forms a brown resin which cannot be crystallised, has a metallic lustre, and is insoluble in water, but very readily soluble in alcohol. The *triacetyl* derivative,  $C_{25}H_{19}SO_8N$ , is a yellow, crystalline powder, and melts at 286°; its constitution is probably represented by the formula  $SO_2 \langle \begin{smallmatrix} NAc \\ C_6H_4 \end{smallmatrix} \rangle C \langle \begin{smallmatrix} C_6H_3(OAc) \\ C_6H_3(OAc) \end{smallmatrix} \rangle O$ .

On saponification, the acetyl compound yields the pure "*saccharein*,"  $SO_2 \langle \begin{smallmatrix} NH \\ C_6H_4 \end{smallmatrix} \rangle C \langle \begin{smallmatrix} C_6H_3(OH) \\ C_6H_3(OH) \end{smallmatrix} \rangle O$ , which crystallises in salmon-coloured scales, melts at 265—267°, dissolves in water and alcohol, and is soluble in alkalis, forming a pure yellow solution, having a green fluorescence; it is reprecipitated as a flocculent mass on the addition of acids. It yields halogen derivatives under the influence of bromine or iodine and sodium chlorate; the *bromo*-derivative is a crystalline powder, insoluble in water, but sparingly soluble in alcohol, which dissolves in alkalis, giving a beautiful red solution; the *iodo*-derivative is an orange-red powder which dissolves in alkalis, giving reddish-violet solutions. The product formed when "*saccharin*" is condensed with diethylmetamidophenol at 165°, is isolated by treating the resulting mass with sodium carbonate and then with soda, the insoluble residue being dissolved in hydrochloric acid. The *hydrochloride* separates in small, green crystals having a metallic lustre, dissolves readily in water, giving a solution which is violet-red and has a yellow fluorescence, but when this is heated to boiling it is decolorised, a flocculent, violet-tinted precipitate being formed.

The free *base*,  $SO_2 \langle \begin{smallmatrix} NH \\ C_6H_4 \end{smallmatrix} \rangle C \langle \begin{smallmatrix} C_6H_3(NEt_2) \\ C_6H_3(NEt_2) \end{smallmatrix} \rangle O$ , is colourless, crystallises from toluene or benzene, melts at 243°, is rather soluble in alcohol, benzene, toluene, and xylene, very readily in chloroform, and is insoluble in light petroleum. The *sulphate* closely resembles the hydrochloride.

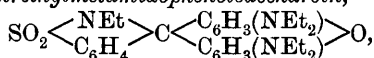
The *saccharein* of *dimethylmetamidophenol* may be made by a method similar to that used in the foregoing case, and its properties resemble those of the corresponding substance; that of *monethylmetamidophenol* has similar properties, but it gives yellower solutions and imparts a colour to unmordanted cotton; it gives a colourless *acetyl* compound. The *saccharein* of *metahydroxydiphenylamine* gives salts which are insoluble in water but dissolve in alcohol, forming a violet-red solution.

*Acetyltetretethylmetamidophenolsaccharein*,



is a colourless, crystalline powder, and may be purified by crystal-

lisation from acetone; it melts at 230—232°, dissolves readily in hot, acidified water, is very soluble in benzene, fairly so in alcohol, chloroform, and ether, and is nearly insoluble in light petroleum; the solution in alcohol or chloroform is red, whilst that in light petroleum or ether is nearly colourless. It is easily saponified by alcoholic soda, the colour of the solution changing to an intense bluish-violet. *Ethyltetrethylmetamidophenolsaccharein*,



made by the action of ethylic iodide and sodium ethoxide on tetrethylmetamidophenolsaccharein, is colourless, dissolves readily in benzene, sparingly in ether and alcohol, and melts at 220—222°. The salts are more unstable than those of the parent substance, being somewhat readily decomposed by boiling water. A. L.

**1:5-Diketones.** By EMIL KNOEVENAGEL (*Annalen*, 1898, 303, 223—257. Compare Abstr., 1896, i, 210).—[With H. HOFFMANN.]—*Ethylic piperonylidenediacetoacetate*,  $\text{C}_{20}\text{H}_{24}\text{O}_8$ , obtained from piperonal and ethylic acetoacetate (2 mols.) in presence of diethylamine, crystallises from alcohol in small, white needles, and melts at 146—147°. Hydroxylamine converts it into the *oxime*  $\text{C}_{20}\text{H}_{23}\text{NO}_7$ , arising from the ethereal salt by elimination of  $2\text{H}_2\text{O}$  and formation of a cyclohexenone ring; it melts and decomposes at 202°. *Ethylic 1-methyl-3-piperonyl-5-cyclohexenone-2:4-dicarboxylate*,  $\text{C}_{20}\text{H}_{22}\text{O}_7$ , produced on passing hydrogen chloride into ethylic piperonylidenediacetoacetate suspended in alcohol, crystallises from alcohol, and melts at 102°. *1-Methyl-3-piperonyl-5-cyclohexenone*,  $\text{C}_{14}\text{H}_{14}\text{O}_3$ , is obtained by the action of boiling, 10 per cent. caustic potash on ethylic piperonylidenediacetoacetate, and crystallises from petroleum in white needles melting at 84—85°; the *oxime* melts and decomposes at 137°.

*Ethylic orthonitrobenzylidenediacetoacetate*,  $\text{C}_{19}\text{H}_{23}\text{NO}_8$ , from ethylic acetoacetate and orthonitrobenzaldehyde, crystallises from alcohol in white needles and melts at 163—164°.

[With ALFRED SCHÜRENBERG.]—*Ethylic metanitrobenzylidenediacetoacetate* melts at 146°; the *oxime* and *phenylhydrazone* melt at 201° and 161° respectively. *1-Methyl-3-metanitrophenyl-5-cyclohexenone*,  $\text{C}_{13}\text{H}_{13}\text{NO}_3$ , is prepared by the action of boiling 40 per cent. sulphuric acid on ethylic metanitrobenzylidenediacetoacetate, which, along with the para-compound, differs from other 1:5-diketones in yielding cyclohexenones under the influence of acids rather than of alkalis; it melts at 98°, whilst the *oxime* and *phenylhydrazone* melt at 176° and 135—150° respectively. *β-Metanitrophenylglutaric acid*,  $\text{C}_{11}\text{H}_{10}\text{NO}_6$ , obtained by the action of moderately heated 5 per cent. caustic soda, melts at 205—206°; prolonged treatment with boiling alkali yields the same product associated with a small quantity of methylnitrophenylcyclohexenone.

[With H. HOFFMANN.]—*Ethylic paranitrobenzylidenediacetoacetate* melts at 170—171°; the *oxime* and *phenylhydrazone* melt at 208° and 214—215° respectively. *Ethylic 1-methyl-3-paranitrophenyl-5-cyclohexenonecarboxylate*,  $\text{C}_{16}\text{H}_{17}\text{NO}_5$ , obtained by treating the foregoing ethereal salt with boiling 20 per cent. sulphuric acid, melts at 119°.



whilst a 40 per cent. solution yields 1-methyl-3-*paranitrophenyl*-5-cyclohexenone, which crystallises from dilute alcohol in white needles, and melts at 134°; the *oxime* and *phenylhydrazone* melt at 179—180° and 173° respectively. *β-Paranitrophenylglutaric acid* separates from alcohol in colourless crystals, and melts at 235°.

[With K. WEDEMEYER.]—*Ethylic cuminyldenediacetoacetate*,  $C_{22}H_{30}O_6$ , melts at 137°. Hydrogen chloride converts it, if suspended in alcohol, into *ethylic 1-methyl-3-isopropylphenyl-5-cyclohexenone-2:4-dicarboxylate*,  $C_{22}H_{28}O_6$ , which crystallises from alcohol and melts at 112°; the *oxime*, which melts and decomposes at 188°, is also obtained by the action of hydroxylamine on *ethylic cuminyldenediacetoacetate*. 1-Methyl-3-isopropylphenyl-5-cyclohexenone melts at 27°, and boils at 210·5 under a pressure of 17 mm.; the *oxime* melts at 124°.

*Ethylic furfuryldenediacetoacetate*,  $C_{17}H_{22}O_7$ , crystallises from petroleum, melts at 72°, and develops an intense violet-red coloration with ferric chloride; the *oxime* of the corresponding cyclohexenone compound obtained by the action of hydroxylamine melts and decomposes at 142°. *Ethylic 1-methyl-3-furfuryl-5-cyclohexenonecarboxylate*,  $C_{14}H_{16}O_4$ , melts at 72°, and boils at 194° under a pressure of 9 mm.; the *oxime* melts at 110—112°. 1-Methyl-3-furfuryl-5-cyclohexenone is a colourless liquid which boils at 153—154° under a pressure of 10 mm.; it has a sp. gr. = 1·1056 at 16°/4°, and the refractive index  $n_D = 1·5354$ . The *oxime* melts at 96—98°.

[With W. GOECKE.]—*Ethylic anisilyldenediacetoacetate*,  $C_{20}H_{26}O_7$ , melts at 137°; hydroxylamine converts it into the *oxime* of the corresponding cyclohexenone compound, which crystallises from alcohol and melts at 195°. *Ethylic 1-methyl-3-paramethoxyphenyl-5-cyclohexenone-2:4-dicarboxylate*,  $C_{20}H_{24}O_6$ , melts at 103°. 1-Methyl-3-paramethoxyphenyl-5-cyclohexenone,  $C_{14}H_{16}O_2$ , melts at 65°; the *oxime* melts at 108°.

[With A. GROOS.]—*Ethylic methylsalicyldenediacetoacetate*,  $C_{20}H_{26}O_7$ , melts at 125°; hydroxylamine converts it into the *oxime* of the corresponding cyclohexenone compound, which crystallises from xylene in stellate aggregates of white needles and melts at 145°. *Ethylic 1-methyl-3-orthomethoxyphenyl-5-cyclohexenone-2:4-dicarboxylate*  $C_{20}H_{24}O_6$ , crystallises from alcohol, and melts at 113°. 1-Methyl-3-orthomethoxyphenyl-5-cyclohexenone,  $C_{14}H_{16}O_2$ , crystallises from petroleum in cubes, and melts at 51°; the *oxime* crystallises from dilute alcohol in white leaflets, and melts at 133°.

[With R. WEISS.]—*Ethylic parachlorobenzilyldenediacetoacetate*,  $C_{19}H_{23}ClO_6$ , crystallises from alcohol in slender, white needles, and melts at 150—151°; hydroxylamine converts it into the *oxime* of the corresponding cyclohexenone, which melts at 187—188°. *Ethylic 1-methyl-3-parachlorophenyl-5-cyclohexenone-2:4-dicarboxylate*,  $C_{19}H_{21}ClO_6$ , melts at 100—101°. 1-Methyl-3-parachlorophenyl-5-cyclohexenone,  $C_{13}H_{13}ClO$ , crystallises from petroleum in colourless needles, and melts at 59—60° to a viscous liquid which boils at 205—206° under a pressure of 12 mm. Hydroxylamine gives rise to two products, the *oxime*,  $C_{13}H_{14}NOCl$ , and the abnormal *oxime*,  $C_{13}H_{17}N_2O_2Cl$ ; these compounds melt at 154° and 197° respectively. M. O. F.

**Hydroxydiphenylene Ketone.** By GEORG HEYL (*Ber.*, 1898, 31, 3033—3035. Compare Staedel, *Abstr.*, 1895, i, 233).—The author has prepared certain derivatives of symmetrical diorthodiamidobenzophenone. The *diacetyl* derivative melts at 154°. *Diorthiodobenzophenone*,  $\text{CO}(\text{C}_6\text{H}_4\text{I})_2$ , crystallises in white, lustrous leaflets, and melts at 106—107°. The *diazo*-compound,  $\text{CO}(\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SO}_4\text{H})_2$ , forms small, white needles and decomposes at 111—112°; it develops a carmine-red coloration with  $\alpha$ -naphthol.

The following derivatives of hydroxydiphenylene ketone are also described. The *oxime* and *phenylhydrazone* melt at 169—170° and 173—174° respectively, whilst the *acetyl* and *benzoyl* derivatives melt at 130—131° and 128—129° respectively. The *benzylic*, *methylic*, and *ethylic* ethers melt at 93—94°, 141.5—142.5°, and 99—100° respectively; the *phenylcarbamate* melts at 148—149°.

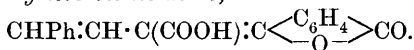
When fused with potash, hydroxydiphenylene ketone yields orthophenylsalicylic acid; the *methylic* salt is an oil, but the *ethylic* salt crystallises in white leaflets and melts at 46—47°.

*Orthophenylmethylosalicylic acid* [2-methoxydiphenyl-1-carboxylic acid],  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Ph}\cdot\text{COOH}$ , and *orthophenylethylsalicylic acid* [2-ethoxydiphenyl-1-carboxylic acid],  $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Ph}\cdot\text{COOH}$ , are liquid. *Hydroxyfluorene alcohol*,  $\text{C}_6\text{H}_4\text{—CH}(\text{OH})\text{—C}_6\text{H}_3\cdot\text{OH}$ , obtained by reducing hydroxydiphenylene ketone, crystallises in white needles melting at 201—201.5°. M. O. F.

**Benzilorthocarboxylic Acid.** By CHARLES A. SOCH (*J. Physical Chem.*, 1898, 2, 364—370).—The author has studied the conditions of equilibrium for the two modifications of benzilorthocarboxylic acid. The yellow modification melts at 141.5°, whilst the white form melts at 125—130°, and changes over to the yellow form; the white modification is stable below 65°, and the yellow crystals are stable between 65° and 132°. The temperature of the unstable eutectic point is about 112°. Raising the initial temperature of heating first lowers and then raises the apparent freezing point. The percentage of the white modification in the melt increases with rising temperature; at some temperature between 65° and 132°, the heat of transformation is zero. H. C.

**Condensation Products of Phenylisocrotonic Acid: Isomeric Lactones of  $\gamma$ -Ketonic Acids.** By JOHANNES THIELE (*Annalen*, 1898, 303, 217—222. Compare Erlenmeyer, jun., and Lux, *Abstr.*, 1898, i, 668).—The paper is a preliminary communication. Phenylisocrotonic acid undergoes condensation with benzaldehyde, yielding *dibenzylidenepropionic acid*,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{:CHPh})\cdot\text{COOH}$ ; cinnamaldehyde gives rise to 1:6-diphenylhexatriene-3-carboxylic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{COOH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}$ ; pyrocinchonic anhydride forms the *lactone*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{CMe} \\ \text{O}\cdot\text{CO} \end{smallmatrix}\text{CMe}$ . Phthalic anhydride yields the *lactone*  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O}\cdot\text{O} \end{smallmatrix}\text{CO}$ , along with two iso-

meric *phthalylphenylisocrotonic acids*,



Bromine converts dibenzylidenepropionic acid into a  *dibromide*, along with the unsaturated *lactone*,  $\text{CHPh}:\text{C}\begin{array}{c} \text{CH} \\ \text{COO} \end{array}\text{CPh}$ , which, on hydrolysis, yields *phenacylcinnamic acid*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{C}(\text{CHPh})\cdot\text{COOH}$ , and this, on reduction, gives rise to *phenacylhydrocinnamic acid*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{COOH}$ . When phenacylhydrocinnamic acid is treated with cold acetic anhydride containing a trace of sulphuric acid, the labile *lactone*,  $\text{CH}_2\text{Ph}\cdot\text{CH}\begin{array}{c} \text{CH} \\ \text{COO} \end{array}\text{CPh}$ , melting at  $100-101^\circ$  is produced; boiling acetic anhydride, however, converts phenacylhydrocinnamic acid into the stable *lactone*,  $\text{CH}_2\text{Ph}\cdot\text{C}\begin{array}{c} \text{CH} \\ \text{COO} \end{array}\text{CHPh}$ , which melts at  $67^\circ$ ; both lactones are resolved by alkalis and by cold glacial acetic acid saturated with hydrogen bromide into phenacylhydrocinnamic acid. The formation of an  $\alpha$ -unsaturated lactone from a  $\gamma$ -ketonic acid, and *vice versa*, throws some doubt on the constitution of lactones hitherto regarded as unsaturated in the  $\beta$ -position.

Desylacetic acid is converted by cold acetic anhydride containing sulphuric acid into a labile *lactone*,  $\begin{array}{c} \text{CH}_2-\text{CO} \\ \text{CPh}:\text{CPh} \end{array}\text{O}$ , which melts at  $100^\circ$ ; hydrolysis with potash regenerates desylacetic acid, whilst boiling acetic anhydride converts it into diphenylcrotonolactone, which melts at  $151.5^\circ$ , and probably has the constitution  $\begin{array}{c} \text{CH}-\text{CO} \\ \text{CPh}:\text{CHPh} \end{array}\text{O}$  (compare Klingemann, Abstr., 1892, 1002). It follows that the conversion of diphenylhydroxybutyrolactone into diphenylcrotonolactone proceeds on simpler lines than those indicated by Erlenmeyer, jun., and Lux (*loc. cit.*); the hydroxy-acid,  $\text{C}_{16}\text{H}_{14}\text{O}_3$ , probably has the constitution  $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}:\text{CH}\cdot\text{COOH}$ .  
M. O. F.

**New Method for Transforming Paranitrodiaminotriphenylmethanes into Rosanilines or their Leuco-bases.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1897, 17, [iii], 654—659).—Paranitrodiamidotriphenylmethane or one of its derivatives is heated on the water-bath with a dilute solution of soda in weak alcohol for about an hour, the alcohol then distilled off, and the product isolated by the addition of lime; it may be transformed into the corresponding rosaniline base by means of a suitable reducing agent.

When the above *product* is reduced with zinc-dust and a mineral acid, it gives a hydroxylamine compound; when dissolved in mineral acid or in acetic acid, it dyes cotton, mordanted with tannin or tartar emetic a bluish-violet; by the action of heat, the solution becomes greyish-blue, and wool or silk immersed in it becomes more or less violet-coloured; in the case of the tetralkyl derivatives, the cotton or silk is dyed a beautiful greenish-yellow. It behaves, therefore, like the basic colouring materials of the rosaniline group, that is to say the paranitro-compound is changed into the carbinol of the base by migra-

tion of an oxygen atom from the nitro-group; on the other hand, the formation of a hydroxylamine compound by its reduction shows that a  $-\text{NO}$  or  $=\text{N}\cdot\text{OH}$  group is still present. Its transformation into rosaniline by means of zinc and acetic acid also indicates the presence of a reducible azoxy-group and a carbinol group.

The constitution of the substance is either  $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\cdot\text{OH}$  or  $\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2\langle\text{C}_6\text{H}_4\rangle\text{N}\cdot\text{OH}$ , the former representing it as a paranitrosocarbinol, and the latter as a derivative of quinoneoxime.

It is found that both substances exist in the product, and the leucobases may be separated by crystallisation. One gram of the leucobase from the tetramethyl derivative is dissolved in water (80 grams) containing soda (10 grams) and alcohol (160 grams), and the whole heated on the water-bath for about half an hour; the liquid, when left to cool for 24 hours, deposits red crystals, whilst, later, yellow crystals separate, the amount being increased by the addition of brine.

The red substance turns brown at  $85^\circ$  and melts at  $100\text{--}105^\circ$ ; the yellow substance melts at  $142\text{--}143^\circ$ . Both compounds afford tetramethylrosaniline by reduction, and yield colouring matters on combination with phenols or alicyclic amines. The red substance dissolves in alcoholic acetic acid, giving a magnificent blue solution, and imparts a greenish-blue tint to cotton mordanted with tannin; the solution when heated gradually becomes a beautiful greenish-yellow. The yellow substance dissolves in acids, giving a nearly colourless solution, but on warming gives the same greenish-yellow solution as that obtained with the red substance. The red substance has the constitution represented by the first of the above formulæ, and the yellow that of the second.

The paper concludes with a brief discussion of the theoretical bearings of the above observations. A. L.

**Condensation of Benzylic Cyanide with Aromatic Aldehydes: Symmetrical Triphenylglutaric Acid.** By MARTIN HENZE (*Ber.*, 1898, 31, 3059—3066).—Victor Meyer has shown (*Abstr.*, 1889, 597) that benzylic cyanide and benzaldehyde interact in presence of sodium ethoxide, forming benzylidenebenzylic cyanide,  $\text{CHPh}\cdot\text{CPh}\cdot\text{CN}$ ; the latter condenses with more benzylic cyanide, affording the nitrile of triphenylglutaric acid,  $\text{CHPh}(\text{CHPh}\cdot\text{CN})_2$ , which may be obtained from benzaldehyde in one step, by employing two molecular proportions of benzylic cyanide. Meta- and para-nitrobenzaldehyde and furfuraldehyde act in a similar way, but in the case of orthonitrobenzaldehyde and cinnamaldehydes, steric hindrance appears to come into play.

*Triphenylglutaronitrile*,  $\text{C}_{23}\text{H}_{18}\text{N}_2$ , which crystallises from a mixture of alcohol and ether in large, well formed crystals belonging to the cubic system, melts at  $137\text{--}138^\circ$ . When heated in a flask at  $320^\circ$ , it is slowly decomposed into benzylidenebenzylic cyanide and benzylic cyanide, a little hydrogen cyanide being also produced. When made in the above manner, it is accompanied by a very small quantity of a second substance, which melts at  $153\text{--}155^\circ$ .

*Triphenylglutaric acid*,  $\text{C}_{23}\text{H}_{20}\text{O}_4$ , is made by heating the nitrile

with fuming hydrochloric acid in closed tubes at 180—200°, when a small quantity of another substance, soluble in alkali, is also formed. It melts at 236—237°, crystallises from dilute alcohol in felted needles containing 1 molecule of alcohol of crystallisation, dissolves in alcohol, acetone, chloroform, and ethylic acetate, but is insoluble in water, benzene, ether, and light petroleum. The *silver* salt,  $C_{23}H_{18}O_4Ag_2$ , blackens slowly when exposed to light.

When attempts are made to hydrolyse triphenylglutaronitrile with alcoholic alkali, hydrolysis occurs, but further decomposition also takes place; in one instance, phenylacetic acid was detected, and an acid melting at 188—190°.

*Triphenylglutaric anhydride*,  $C_{23}H_{18}O_3$ , made by dissolving the acid in acetic chloride, exists in two forms; the first *modification*, obtained by the spontaneous evaporation of the acetic chloride solution crystallises in rectangular tablets and melts at 198—199°, whilst the second *modification*, produced when the first is boiled with acetone, crystallises in needles, and does not melt sharply, but sinters above 170° and is melted at 180°. The transformation of the latter into the former is effected by fusion or by dissolution in acetic chloride; both modifications afford the triphenylglutaric acid melting at 235—236°.

When hydrogen chloride is passed into a solution of triphenylglutaronitrile in dilute alcohol, one cyano-group appears to suffer partial hydrolysis. The *product* crystallises from alcohol, and on analysis gives numbers agreeing with the formula  $CN \cdot CHPh \cdot CHPh \cdot CHPh \cdot CONH_2$ . *Ethylic triphenylglutarate*,  $C_{27}H_{28}O_4$ , made by treating the free acid with alcohol and hydrogen chloride, is difficult to purify and melts at 95—110°.

When triphenylglutaronitrile is reduced with sodium and absolute alcohol, the products obtained are dibenzyl, phenylethylamine, and hydrogen cyanide; these probably result from an initial severance of the molecule, under the influence of alkali, into  $CHPh \cdot CPh \cdot CN$  and  $CH_2Ph \cdot CN$ , the former, by union with 4 atoms of hydrogen, affording  $CH_2Ph \cdot CH_2Ph$  and  $HCN$ .  
A. L.

**Anhydrobisdiketohydrindene (Bindone).** By WILHELM WISLIZENUS (*Ber.*, 1898, 31, 2935—2938).—In reply to Ephraim (*Abstr.*, 1898, i, 672), the author points out that the yellow compound described by himself and Reitzenstein (*Abstr.*, 1894, i, 133) is only formed when anhydrobisdiketohydrindene is heated with acetic anhydride or alcoholic hydrogen chloride, and that it decomposes at 290—295°. It is not identical with the yellow compound formed when diketohydrindene is heated with the anhydro-derivative, and when the red condensation product of the latter is recrystallised from pyridine or boiled with alcohol. The author proposes to term the anhydro-compound *bindone*.  
A. H.

**Colour Reactions of Indones and of Quinones with Malonic Acid Derivatives.** By CARL LIEBERMANN (*Ber.*, 1898, 31, 2903—2907. Compare *Abstr.*, 1898, i, 682).—Dibromindone reacts with ethylic sodiomalonate, yielding ethylic bromindonemalonate,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CBr} \end{smallmatrix} \text{C} \cdot \text{CH}(\text{COOEt})_2$ , which in alkaline solution has a deep red colour. Dichloro- and dibromo-cinnamic acids do not yield similar products, but cyclic compounds, such as 2:3-dibrom- $\alpha$ -naphthaquinone, react yielding cornflower-blue products; but as these are unstable in alkaline solution, it is necessary to precipitate immediately with acetic acid. The product from 2:3-dibrom- $\alpha$ -naphthaquinone crystallises from alcohol in yellow needles which turn blue on the addition of a trace of alkali.

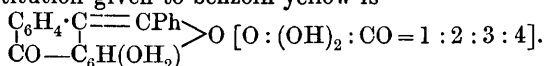
Dibromo- $\beta$ -naphthaquinone yields a bluish-green solution with ethylic sodiomalonate, which, when acidified, yields a resinous compound crystallising from alcohol in orange-yellow needles; monobromo- and monochloro- $\beta$ -naphthaquinone behave in a similar manner. The colours are, as a rule, extremely evanescent in alkaline solution, and rapidly become destroyed. Chlorinated quinones also react with malonic acid derivatives in a similar manner (compare Stieglitz, *Abstr.*, 1891, 455; Jackson and Grindley, *Abstr.*, 1893, i, 563), as also do the simple quinones themselves. Benzoquinone, with a solution of ethylic sodiomalonate, yields evanescent colours;  $\alpha$ -naphthaquinone gives a greenish-blue, and  $\beta$ -naphthaquinone a red colour. J. J. S.

**2-Bromoflavone.** By STANISLAUS VON KOSTANECKI and A. LUDWIG (*Ber.*, 1898, 31, 2951—2953).—5-Bromo-2-acetoxybenzylideneacetophenone,  $\text{OAc} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$ , obtained when the corresponding hydroxy-compound (*Abstr.*, 1898, i, 371) is heated with acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in colourless needles melting at 115—116°, and yields a dibromide,  $\text{C}_{17}\text{H}_{13}\text{Br}_3\text{O}_3$ , which crystallises from alcohol in glistening plates melting at 121—122°. The dibromide, when treated with the requisite quantity of potassium hydroxide solution and then poured into water,

yields a flocculent precipitate of 2-bromoflavone,  $\text{C}_6\text{H}_3\text{Br} \begin{smallmatrix} \text{O} - \text{CPh} \\ | \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ , which crystallises from alcohol in colourless needles melting at 189—190°, and dissolves in concentrated sulphuric acid, yielding a colourless, non-fluorescent solution. Flavone itself, when quite pure, also gives a colourless solution with sulphuric acid, but this exhibits a marked violet-blue fluorescence, the former statement (*Abstr.*, 1898, i, 584) being incorrect. Bromoflavone, when hydrolysed with a concentrated solution of sodium ethoxide, yields benzoic acid and 5-bromo-2-hydroxyacetophenone. J. J. S.

**Benzoin Yellow.** By CARL GRAEBE (*Ber.*, 1898, 31, 2975—2979).—The author has investigated the yellow dye obtained by the condensation of benzoin with gallic acid (D.R.P. 95739, *Chem. Centr.*, 1898, i, 870). To prepare it, benzoin is added to a solution of gallic acid in sulphuric acid (66° B) kept at 0—5° and after being stirred during 24 hours, the mixture is poured into water, when the dye is precipitated; it crystallises from a mixture of alcohol and acetic acid in yellow needles, decomposes at about 250°, is readily soluble in sodium hydroxide, and dissolves slowly in sodium carbonate solution. The acetyl derivative,  $\text{C}_{21}\text{H}_{10}\text{O}_4\text{Ac}_2$ , crystallises in pale yellow needles melting at 237°. The lead salt, when dried at 150°, has the composi-

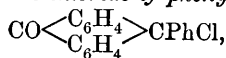
tion  $C_{21}H_{10}O_4Pb$ . Benzoin-yellow, when distilled with zinc dust, yields anthracene, and, when oxidised with nitric acid (sp. gr. = 1.3), yields benzoic and phthalic acids in nearly equal quantities. When fused with sodium hydroxide, it yields benzoic acid, and when suspended in chloroform and treated with bromine gives a *dibromide* which crystallises from acetic acid and decomposes at 221—222°. The constitution given to benzoin yellow is



J. J. S.

**Action of Hydrazine Hydrate on Phenols.** By L. HOFFMANN (*Ber.*, 1898, 31, 2909—2910).—When  $\alpha$ - or  $\beta$ -naphthol is heated with excess of hydrazine hydrate for 6 hours at 160°,  $\alpha$ - or  $\beta$ -naphthylhydrazine is formed. With phenol, the condensation takes place less easily; at 160°, only phenoldiammonium,  $C_6H_5 \cdot OH, N_2H_4$  (Curtius and Thun, *J. pr. Chem.*, 1876, [ii], 14, 190) is formed, but at 220° a small quantity of phenylhydrazine is obtained. C. F. B.

**Syntheses by means of Orthophthalyl Tetrachloride (m. p. 88°).** I. **Preparation of Diphenylanthrone.** By ALBIN HALLER and ALFRED GUYOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 873—879).—*Diphenylanthrone*,  $CO < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CPh_2$ , is prepared by the action of aluminium chloride on a solution in benzene of phthalyl tetrachloride (m. p. 88°); the chlorides of anthraquinone and of phenyloxanthranol are intermediate products, and can be used for preparing the substance. The authors ascribe to the phthalyl tetrachloride the formula  $CCl_3 \cdot C_6H_4 \cdot COCl$ , and as small quantities of diphenylanthrone are produced in the condensation of commercial phthalyl dichloride with benzene, it is probable that the dichloride contains a certain amount of this tetrachloride. Diphenylanthrone melts at 192°, crystallises from glacial acetic acid in colourless needles and from benzene in large, transparent prisms, is insoluble in water, and dissolves only slightly in boiling alcohol, ether, and light petroleum. The molecular weight, as determined by the cryoscopic method, was 320 to 325 (calc. 346). The substance does not react with phenylhydrazine or with hydroxylamine; on crystallising from nitrobenzene, large, transparent tablets of a pale yellow colour are obtained, which have the composition  $2C_{26}H_{18}O + C_6H_5 \cdot NO_2$ . The *chloride of phenyloxanthranol*,



prepared by warming diphenylphthalide with phosphorus pentachloride, crystallises from benzene in large, colourless, transparent prisms, and melts at 164°. When heated with water in sealed tubes, it is converted quantitatively into phenyloxanthranol, whilst with alcohols it yields the corresponding ethers. T. M. L.

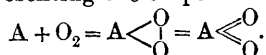
**The Rendering Active ("Activirung") of Oxygen.** II. **The Active Oxygen of Oil of Turpentine.** By CARL ENGLER and J. WEISSBERG (*Ber.*, 1898, 31, 3046—3055).—Pure pinene is oxidised

by air or oxygen in exactly the same way as is crude turpentine. The chemical activity of turpentine exposed to oxygen does not depend on the formation of ozone or of atomic oxygen, as the substance retains its properties for years if kept in the dark, which would not be the case if such powerful oxidising substances were present. Berthelot has shown that only the dissolved oxygen is driven out when inert gases are led through the active liquid (*Ann. Chim. Phys.*, 1860, [iii], 58, 426), and it is found that the residue left after distilling the greater part of the pinene in a vacuum still has strong oxidising powers. The substance gives a yellow coloration with a solution of titanous acid in sulphuric acid, and a brown coloration with vanadic acid, reactions which are exhibited by most peroxides, but not with ozone. If, moreover, oxidising substances of this kind owed their activity to active oxygen, their oxidising powers should be similar, which is by no means the case.

The activity cannot, on the other hand, be due to the presence of hydrogen peroxide, for Kingzett (this Journ., 1874, 511; 1875, 210) has shown that the active substance cannot be extracted by water, and Löw has observed (*Zeit. f. Chem.*, [ii], 6, 609) that iodine is liberated when oxidised turpentine is shaken with a solution of potassium iodide, a reaction not shown by hydrogen peroxide. It is now found that it does not afford the characteristic blue solution when shaken with chromic acid solution and ether, whilst an equivalent amount of hydrogen peroxide, added to turpentine and treated in the same manner, gives a decided indication of its presence. The presence of hydrogen peroxide, observed by most experimenters, is doubtless due to the presence of water in the original oil. It is not necessary, however, that water should be present, as turpentine which has been dried by means of sodium and phosphorus pentoxide rapidly absorbed dry oxygen.

The activity of the oil is not proportional to the amount of oxygen absorbed, hence a certain quantity of the latter is used up in a more profound oxidation of the turpentine. Experiments made on the action of oxygen on turpentine at various temperatures have shown that, at about 100°, the oil is rendered active most rapidly, and that, at 140–160°, the active oxygen disappears, being, doubtless, used up in the further oxidation of the substance, an action which also goes on slowly at 80–100°.

The authors express their views of the actions which go on in the following manner, representing the turpentine by A.



If the second of these changes is not intramolecular, but intermolecular, unaltered turpentine being attacked, the equation then becomes  $AO_2 + A = 2AO$ .

The action of the peroxide,  $A \begin{array}{c} \diagup O \\ \diagdown O \end{array}$ , on easily oxidisable substances is represented as  $AO_2 + B = AO + BO$ .

The action of water on peroxides is briefly discussed, and the



production of hydrogen peroxide is attributed to formation of an intermediate hydrate which affords hydrogen peroxide by intramolecular change.

A. L.

**Citral (Geranial) and Lemon-grass Oil.** By FRIEDRICH W. SEMMLER (*Ber.*, 1898, 31, 3001—3003).—The author says "Stiehl's citriodorlaldehyde, as well as his geranial and allolemonal (this vol., i, 66) yielded in my hands, when sufficiently purified, one and the same geranial, with absolutely identical physical properties, and with identical derivatives. . . . I must still maintain the identity of citral with the geranial obtained by me by oxidising geraniol."

C. F. B.

**Citral.** By OSCAR DOEBNER (*Ber.*, 1899, 31, 3195—3197).—The author has shown that lemon-grass oil contains 80—82 per cent. of citral (*Abstr.*, 1898, i, 676); according to Stiehl, however (this vol., i, 66), the oil contains three isomeric aldehydes, namely, citral (10 per cent.), citriodorlaldehyde (40—50 per cent.) and allolemonal (25—30 per cent.). In view of this discrepancy, the author has examined the portions of the oil to which the last two names are given by Stiehl. "Citriodorlaldehyde" is nearly pure citral, as when treated with pyruvic acid and  $\beta$ -naphthylamine it gives a large quantity of citryl- $\beta$ -naphthacinchonic acid, together with a small quantity of a second acid which melts, while still impure, at 230°. Allolemonal consists of a mixture of about equal parts of aldehydic and non-aldehydic constituents, and the former, after separation by the bisulphite method and treatment with pyruvic acid and  $\beta$ -naphthylamine, gives only citryl- $\beta$ -cinchonic acid. Crude allolemonal gives also methylcinchonic acid and another acid which is sparingly soluble in alcohol, and melts indefinitely at 210—235° (Stiehl gives the melting point of allolemonyl- $\beta$ -naphthacinchonic acid as 235°); this impure acid resolves itself on recrystallisation into the citrylic acid, methyl- $\beta$ -naphthacinchonic acid, and probably, also, a neutral condensation product of pyruvic acid and  $\beta$ -naphthylamine, melting at 232°, which is easily obtained by warming them together in alcoholic solution for a short time. The author's former results are therefore completely confirmed.

A. L.

**Orientation in the Terpene Series. XXIII. Hydroxycarone and Ketoterpin.** By ADOLF VON BAEYER and CONRAD BAUMGÄRTEL (*Ber.*, 1898, 31, 3208—3217).—Optically active 1:8-hydroxybromotetrahydrocarvone is obtained as its sodium derivative when Wallach's brominated dihydrocarvone hydrobromide (1:8-dibromotetrahydrocarvone, *Abstr.*, 1894, i, 536) is diluted with ether and shaken with sodium hydroxide (sp. gr. = 1.23) for about an hour. The sodium salt is decomposed with dilute sulphuric acid, and the hydroxybromotetrahydrocarvone rapidly filtered, as it is converted both by water and dilute acid into ketoterpin. When recrystallised from dry ether or a mixture of amylene and light petroleum, it is obtained in large prisms, melts at 69—72°, is readily soluble in most solvents, and is somewhat unstable, being decomposed both by acids

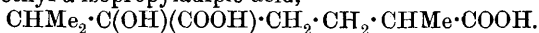
and alkalis. When recrystallised from methylic alcohol, a small quantity of a substance melting at  $136-138^{\circ}$  is obtained, and this contains the same amount of bromine as the hydroxybromo-compound. An active *hydroxycarone*,  $C_{10}H_{16}O_2$ , formed when hydroxybromotetrahydrocarvone (1 mol.) is treated with a solution of potassium hydroxide (1.5 mols.) in methylic alcohol, is a viscous oil distilling at  $134-135^{\circ}$  under 19 mm. pressure, and dissolves somewhat readily in water, the solution having a feebly acid reaction; with concentrated caustic soda, it gives crystals of the sodium derivative. Its *oxime* forms large, glistening prisms melting at  $138^{\circ}$ ; its *semicarbazone*, glistening needles melting at  $197^{\circ}$ , and its *phenylurethane* crystallises from alcohol in four-sided prisms melting and decomposing at  $190^{\circ}$ . The carone ring in hydroxycarone is readily ruptured, even in the cold, by dilute acids; hydrobromic acid gives Wallach's *d*-dibromotetrahydrocarvone, whilst hydrochloric acid gives the corresponding dichloro-derivative melting at  $41-42^{\circ}$ .

*Optically active ketoterpin* is readily obtained when hydroxycarone is gradually treated with ice cold dilute sulphuric acid, the solution neutralised with sodium carbonate, and extracted with ether and alcohol; it crystallises from ether in prisms, melts at  $78-80^{\circ}$ , distils at  $163-165^{\circ}$  under a pressure of 16 mm., and dissolves readily in water, alcohol, or chloroform, but when pure is only sparingly soluble in ether; a 37 per cent. alcoholic solution has a rotatory power  $= -32.5^{\circ}$ . The same compound can also be obtained directly from hydroxybromotetrahydrocarvone. When boiled with dilute sulphuric acid, it is completely converted into carvacrol. Its *sodium* derivative,  $C_{10}H_{17}O_3Na$ , crystallises in small needles, and is reconverted into the ketoterpin by water or alcohol; its *oxime*,  $C_{10}H_{19}NO_3$ , melts at  $163^{\circ}$ ; its *semicarbazone* at  $184-185^{\circ}$ , and its *phenylhydrazone* melts and decomposes at  $150-160^{\circ}$ .

When reduced with sodium and alcohol, ketoterpin yields 1:2:8-*trihydroxyterpan*, which, when distilled under diminished pressure and recrystallised from ether or chloroform, forms six-sided plates melting at  $97-98^{\circ}$ , and readily soluble in water, alcohol, &c. A 20 per cent. alcoholic solution has a rotatory power of  $-55^{\circ}$ . When oxidised with chromic anhydride and sulphuric acid, the trihydroxy-compound yields an active methyl ketone of homoterpenylic acid melting at  $48-49^{\circ}$ .

J. J. S.

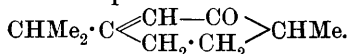
**Carvenone.** By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1898, 31, 2889—2899).—When carvenone, which, according to the authors, is most readily obtained by Baeyer's method (*Abstr.*, 1894, i, 535), is oxidised with a 2 per cent. alkaline solution of potassium permanganate (3 atoms of oxygen to 1 molecule of carvenone), the chief products are,  $\alpha$ -methylglutaric acid, 2:6-dimethylheptan-5-onoic acid,  $CHMe_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot COOH$ , and  $\alpha$ -hydroxy- $\alpha'$ -methyl- $\alpha$ -isopropyladipic acid,



From 40 grams of carvenone, about 36 grams of the mixed acids are obtained, lower fatty acids are removed by distillation with steam,

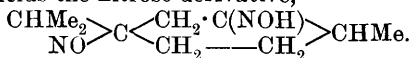
and the residue dissolved in ether and extracted several times with an amount of sodium carbonate solution insufficient to neutralise all the acid present. The first extracts contain the stronger acids, the neutral solution of these is boiled with excess of copper acetate when the sparingly soluble copper salt of  $\alpha$ -methylglutaric acid is precipitated. The filtrate, when acidified, yields  $\alpha$ -hydroxy- $\alpha'$ -methyl- $\alpha$ -isopropyl-adipic acid, which is the chief oxidation product, and when freed from acetic acid gradually solidifies; after repeated crystallisation from water, it melts at  $136-137^\circ$ . It yields a sparingly soluble *silver* salt, and when heated just above its melting point loses water and yields a *lactonic acid*,  $C_{10}H_{16}O_4$ , melting at about  $100^\circ$ . When gently oxidised, the acid,  $C_{10}H_{18}O_5$ , is converted into 2:6-dimethylheptan-4-onoic acid. The latter acid is also obtained from the last sodium carbonate extracts, as it is a very feeble acid; it is an oil, and does not solidify at  $-20^\circ$ , but distils at  $166-168^\circ$  under 14 mm. pressure. It yields an *oximido*-derivative,  $C_9H_{16}O_2 \cdot N \cdot OH$ , melting at  $67-68^\circ$ , and sparingly soluble in water. When further oxidised, it yields acetone and  $\alpha$ -methylglutaric acid.

The constitution of carvenone which is most in harmony with the formation of these oxidation products is



Wallach's hydroxylamine derivative melting at  $162-163^\circ$  would

then have the constitution  $\begin{array}{c} CHMe_2 \\ HO \cdot NH \end{array} > C \begin{array}{c} CH_2 \cdot C(NO)H \\ CH_2 - CH_2 \end{array} > CHMe_2$ , and when oxidised yields the nitroso-derivative,



J. J. S.

**Solubility of Camphor.** By CONSTANTIN I. ISTRATI and AL. J. ZAHARIA (*Compt. rend.*, 1898, 127, 557-559).—Camphor, contrary to the usual statements, is slightly soluble in water; a saturated solution has a sp. gr. = 1.00071 at  $15^\circ$ , and, in a tube 22 cm. long is dextrorotatory  $[\alpha]_D = +0.4^\circ$ . In concentrated hydrochloric acid, camphor dissolves much more readily at  $0^\circ$  than at higher temperatures; 100 c.c. of a saturated solution contains, at  $0^\circ$ , 40.276 grams of camphor. On warming the solution by the heat of the hand, camphor is deposited, but, on again cooling, this redissolves; on diluting the solution, camphor separates. It is suggested that camphor probably dissolves in concentrated hydrochloric acid owing to the formation of the compound  $C_8H_{14} \begin{array}{c} \text{CCl} \cdot OH \\ | \\ CH_2 \end{array}$ , and that this is decomposed either by heat or by the addition of water.

W. A. D.

**Oxidising Action of  $\alpha$ -Chlorocamphor.** By H. VITTENET (*Bull. Soc. Chim.*, 1897, [iii], 17, 705).—When  $\alpha$ -chlorocamphor is heated at  $200^\circ$  with aromatic amines, it undergoes decomposition, the bases being oxidised, with formation of small quantities of the usual characteristic colouring matters. Thus a mixture of toluidine and xylidine gives a magenta, diphenylamine gives diphenylamine-blue,  $\alpha$ -naphthylamine affording  $\alpha$ -naphthamein.

A. L.

**Picrotoxin.** By RICHARD JOS. MEYER and P. BRUGER (*Ber.*, 1898, 31, 2958—2974. Compare Paternò and Ogialoro, this Journal, 1877, i, 719; ii, 790; Abstr., 1879, 729; 1881, 440; Barth and Kretschy, Abstr., 1881, 286; 1882, 412; 1884, 846; Schmidt, Abstr., 1881, 740; 1884, 845).—Pikrotoxin is an astringent principle of the fruit of *Menispermum cocculus*. The commercial product usually melts between 192° and 200°, but after recrystallisation from water invariably yields a product melting at 199—200°; it is extremely bitter and very poisonous, producing similar effects to those obtained with strychnine. Paternò and Ogialoro, Schmidt, and others regard it as a definite compound which is readily decomposed into pikrotoxinin and pikrotoxin, but, according to the authors, it is merely a mixture of these two in definite, but not molecular, proportions, namely, 54—55 per cent. of pikrotoxinin and 45—46 of pikrotoxin. It may be partially separated into the two constituents by boiling with benzene or chloroform, or by treatment with barium hydroxide; the only method which gives anything like quantitative results is that with bromine water.

Pikrotoxinin,  $C_{15}H_{16}O_6$ , is best obtained from pikrotoxin by brominating the latter, when in hot aqueous solution, with a slight excess of bromine water, and then, by means of zinc dust and acetic acid, removing the bromine from the monobromopikrotoxinin, which crystallises out; it crystallises from hot water in colourless, anhydrous needles, but from cold aqueous solutions in rhombic plates containing  $1H_2O$ , melts at 200—201°, is readily soluble in all the usual solvents on warming, and also in cold alcohol or chloroform; it is also soluble in alkalis, but is not reprecipitated on the addition of acids. Sulphuric acid develops an intense orange-red coloration, and when hydrogen chloride is led into an ethereal solution of the compound, polymerisation occurs, and *pikrotoxide*, melting at 308—310°, is formed. Aqueous solutions reduce ammoniacal silver nitrate in the cold, but it contains neither an aldehydic nor a ketonic group. It has an extremely bitter taste, and is the active principle of pikrotoxin; its specific rotatory power  $[\alpha]_D = -5.85^\circ$ .

Bromopikrotoxinin,  $C_{15}H_{15}BrO_6$ , which is most readily obtained by adding bromine water to a hot, nearly saturated aqueous solution of pikrotoxinin until the solution remains permanently yellow, may be purified by recrystallisation from absolute alcohol; it separates in glistening needles, melts at 259—260° (Schmidt gives 250—255°; Paternò and Ogialoro give 240—250°), and has  $[\alpha]_D^{17} = -132.5^\circ$ .

*Chloropikrotoxinin* crystallises from alcohol in a mixture of needles and plates melting at 272°.

*Iodopikrotoxinin*, obtained by the action of iodic acid and a solution of iodine in potassium iodide on a hot aqueous solution of pikrotoxinin, crystallises from alcohol in colourless needles and melts at 198—199°.

*Bromopikrotoxic acid*,  $C_{14}H_{16}BrO_5 \cdot COOH + H_2O$ , is obtained when 10 per cent. potassium hydroxide solution is slowly added to finely divided bromopikrotoxinin suspended in 10 times its weight of boiling water until all has dissolved; on the addition of hydrochloric acid, the acid crystallises out in colourless needles melting at

245—246°; it has no bitter taste and is optically active  $[\alpha]_D = -62.6^\circ$ . The *calcium* salt,  $(C_{15}H_{18}BrO_7)_2Ca + 5H_2O$ , *potassium* salt, with  $2H_2O$ , *ammonium* salt, and *mercurous* salt have been prepared. *Pikrotoxic acid*,  $C_{15}H_{18}O_7$ , obtained in small amount by the removal of bromine from the bromo-acid by the aid of sodium amalgam in alkaline solution, crystallises from water in needles melting at 229—230°, and has no bitter taste; its aqueous solution has strong reducing properties, and it readily undergoes decomposition in both aqueous and ethereal solution.

The substance obtained by Paternò and Ogliaro by the action of sodium acetate and acetic anhydride on pikrotoxin and described as an unsaturated acid, is shown to be *diacetylpikrotoxinin*,  $C_{15}H_{14}O_6Ac_2$ , as it can readily be obtained by the action of acetic chloride on pikrotoxinin; it sublimes in slender needles melting at 254—255°, and forms an unstable compound with bromine.

Pikrotoxin,  $C_{15}H_{18}O_7$ , is best obtained from the filtrate from bromopikrotoxinin, part separating out on cooling, whilst the remainder may be obtained by evaporation; it can be purified by several extractions with small quantities of hot chloroform, followed by recrystallisation from water; it forms small, felted needles, or thick, rhombic prisms melting at 248—250°, is readily soluble in absolute alcohol or acetic acid, but only sparingly in ether, chloroform, or benzene. Its specific rotatory power  $[\alpha]_D = -64.7^\circ$ , and it reduces Fehling's solution, &c., but only on warming. Its molecular formula has been established by molecular weight determinations and by the analyses of its benzoyl and acetyl derivatives.

*Benzoylpikrotoxin*,  $C_{15}H_{17}O_7Bz$ , crystallises from absolute alcohol in colourless needles, melts at 236°, and is readily soluble in chloroform, sparingly in ether or alcohol.

*Dibenzoylpikrotoxin*, obtained when pikrotoxin (1 mol.) is heated with benzoic chloride (3 mols.) at 190°, crystallises from alcohol in needles melting at 247—248°. When a large excess of benzoic chloride is employed, no definite product is obtained.

*Acetylpikrotoxin*,  $C_{15}H_{17}O_7Ac$ , crystallises from benzene, alcohol, or acetic acid in glistening plates melting at 244—245°, and is probably identical with the compound described by Paternò and Ogliaro as *diacetylpikrotoxinin* and melting at 227°. When pikrotoxin is allowed to remain in contact with acetic chloride for 24 hours at the ordinary temperature, and then heated until complete solution ensues, two compounds are obtained. *Anhydrodiacetylpikrotoxin*,  $C_{15}H_{14}O_6Ac_2$ , which is precipitated, on the addition of alcohol, in crystalline masses melting above 300°, and *diacetylpikrotoxin*,  $C_{15}H_{16}O_7Ac_2$ , which is obtained as an oil from the alcoholic mother liquor; when its hot, aqueous solution is allowed to cool, drops of oil separate, which solidify to crystalline needles melting at 207—210°; these contain  $2H_2O$ .

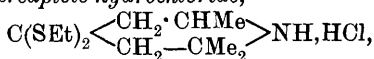
Attempts to convert pikrotoxin into pikrotoxinin by removal of the elements of water have not proved successful.

When warmed with fuming nitric acid, pikrotoxin yields a nitro-derivative,  $C_{15}H_{15}O_6 \cdot NO_2$ , *anhydronitropikrotoxin*, melting at 260°.

J. J. S.

**Chlorophyll and its Derivatives.** By FRIEDRICH G. KOHL (*Chem. Centr.*, 1898, i, 992; from *Bot. Centr.*, 19, 417—426).—The author prepares Schunk's phyllotaonin by treating the green solution obtained by allowing blades of grass to remain immersed in alcoholic potassium hydroxide solution for a long time, with barium nitrate, filtering and washing the precipitate with boiling water, and then with boiling alcohol. The precipitate, unlike Schunk's phyllotaonin, is insoluble in alcohol, and the solution of pure chlorophyll-hydrochloric acid obtained from it by suspending it in water, treating with excess of hydrochloric acid, and precipitating the barium with sulphuric acid, does not yield the alkylic ether of phyllotaonin prepared by Schunk and Marchlewski. According to the author, phyllotaonin is a sodium compound of chlorophyll, and phylloxanthin is not a derivative of chlorophyll. E. W. W.

**Condensation of Cyclic Acetone Bases with Mercaptans; Exceptions to the Rule of Mercaptole Formation.** By HERMANN PAULY (*Ber.*, 1898, 31, 3145—3151).—Vinylidiacetonamine reacts in the normal manner with ethylic and phenylic mercaptans. *Trimethylpiperidinediethylmercaptole hydrochloride*,



formed by the action of vinylidiacetonamine on ethylic mercaptan, crystallises, with  $1\text{H}_2\text{O}$ , in rectangular plates, whilst the anhydrous salt melts at  $161-163^\circ$ , and the free base is an oil. The mercaptole is readily converted by oxidation into *trimethylpiperidinediethylsulphonal*,  $\text{C}(\text{SO}_2\text{Et})_2 \begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CMe}_2 \end{array} \text{NH}$ , which forms small, feathery crystals melting at  $135^\circ$ ; the *hydrochloride* and *platinochloride* are both crystalline. *Trimethylpiperidinediphenylmercaptole hydrochloride* crystallises in plates melting at  $227^\circ$ , whilst the free base melts at about  $78^\circ$  and forms sparingly soluble salts.

Triacetoneamine, on the other hand, only reacts with 1 mol. of ethylic mercaptan, forming *triacetonineethylsulphide hydrochloride*,  $\text{SEt} \cdot \text{C} \begin{array}{c} \text{CH} - \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CMe}_2 \end{array} \text{NH, HCl}$ , which forms small, rhombic crystals melting at  $186^\circ$ ; the free base is a colourless oil, and the *platinochloride* crystallises in slender, yellowish needles. *Triacetonephenylsulphide hydrochloride* crystallises in slender prisms melting at  $187-188^\circ$ ; the free base is a colourless oil, but it unites with  $1\text{H}_2\text{O}$  to form a hydrate which crystallises in prisms often a centimetre in length. It appears probable that this remarkable difference between the closely allied compounds, vinylidiacetonamine and triacetoneamine, depends in some way on the difference in configuration of the groups immediately adjacent to the imido-group. A. H.

**Pyridylacetylchloride and Acetylpyridine.** By ERNST SCHMIDT and DANIEL KNUTTEL (*Arch. Pharm.*, 1898, 236, 580—601. Compare this vol., i, 4).—Pyridylacetylchloride was prepared according to Dreser's directions (*Abstr.*, 1894, i, 549) from pyridine and monochloroacetone. Its *platinochloride* crystallises in dark orange

prisms melting at 206—207°, and its *aurichloride* in yellow needles melting at 141—143°. The *mercurichloride* crystallises in needles melting at 120°, but the double salts with copper and calcium chlorides are not well characterised substances.

When distilled with a solution of sodium carbonate, pyridylacetonyl chloride is converted into its components; with moist silver oxide or when heated alone, it undergoes a complicated decomposition with production of pyridine, and when acted on with sodium amalgam no piperidine derivative has so far been obtained.

*Pyridylacetonyl chloride phenylhydrazone*, prepared by heating together phenylhydrazine, and the chloride, separates from light petroleum in bunches of crystals melting at 133—134°. The *oxime* forms long, white, prismatic crystals melting at 182—184°; it does not reduce Fehling's solution, and gives a *platinochloride* melting at 204—205° with partial decomposition, and an *aurichloride* melting at 144—145°. The *oxime* is more stable towards silver oxide than pyridylacetonyl chloride, and attempts to bring about a rearrangement led to the following results. Concentrated hydrochloric and sulphuric acids decompose the *oxime* into its components; acetic chloride does not act on the *oxime* when heated under pressure, but when heated on a water-bath, it gives rise to a liquid *monacetyl* derivative, yielding an *aurichloride* melting at 140—141°, and a *platinochloride* melting at 195—197°; acetic anhydride converts the *oxime* into hydroxylamine and pyridineacetone chloride, and benzoic chloride or benzoic anhydride decompose it into its components.

When the *oxime* is reduced with sodium amalgam, pyridylacetonyl chloride is reformed, and when heated with ammonium formate, an amine is not produced, but a complicated reaction takes place with production of pyridine.

When piperidine and chloroacetone are heated together in benzene solution, piperidine hydrochloride and a small amount of *acetonyl-piperidine*,  $C_8H_{15}NO$ , are produced; the latter yields an *aurichloride* in clear, yellow crystals melting at 106—107°, and a *platinochloride* in small, prismatic crystals melting at 179—180°.

*Methylpiperidineacetonyl chloride*,  $C_5NH_{10}MeCl \cdot CH_2 \cdot COMe$ , is obtained by the interaction of chloroacetone and methylpiperidine. Its *aurichloride* melts at 86°, and the *platinochloride* crystallises in beautiful orange needles melting at 197—198°. A. W. C.

**Formation of Chains. XXIX. Piperidine.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 2839—2847).

[With STEFANOWSKI].—*Ethylpiperidylacetate*,  $C_5NH_{10} \cdot CH_2 \cdot COOEt$ , obtained when ethylic chloroacetate is added to piperidine, or when benzene solutions of the two are mixed, is separated from the piperidine hydrochloride by the aid of ether, and forms an oil distilling at 209° under 732 mm. pressure. It is hydrolysed when heated with twice its weight of dry barium hydroxide in a salt bath for 10 hours. The acid, when recrystallised from chloroform and alcohol, forms well-developed, colourless prisms, part of which melts at 123—125°, and the residue remains solid even at 211°, this is due to the loss of water, as when dried at 125° the compound has the composition  $C_7H_{13}NO$ .

and then melts at 215—217°. Piperidyloacetic acid is soluble in water, alcohol, chloroform, and also in alkalis and acids.

[With MAISEL.]—Piperidine hydrobromide crystallises in oblong, rhombic plates melting at 235°.

*Ethylic piperidyl- $\alpha$ -propionate*,  $C_5NH_{10} \cdot CHMe \cdot COOEt$ , is a colourless oil distilling at 217°; when hydrolysed with barium hydroxide, it yields  $\alpha$ -piperidylpropionic acid, which crystallises from absolute alcohol, with  $3H_2O$ . After drying at 100°, it melts at 205—206.5°, and is identical with Brühl's piperidyl- $\alpha$ -alanine (this Journ., 1876, i, 699). When heated at 222—240°, the acid evolves carbonic anhydride, and an oil, probably ethylpiperidine, is obtained; at temperatures above 240°, carbonic oxide is evolved, and an alkaline product melting at about 80° left.

[With KUSZELL.]—*Ethylic piperidyl- $\alpha$ -butyrate*,  
 $C_5NH_{10} \cdot CHEt \cdot COOEt$ ,

best obtained by treating ethylic  $\alpha$ -bromobutyrate (1 mol.) with an excess of piperidine (3 mols.), is a colourless oil boiling at 222—223° under 753 mm. pressure. The free acid, after purification by dissolving it in alcohol and precipitating with ether, crystallises from water, with  $\frac{1}{2}H_2O$ , and melts at 106—107°; when dehydrated at 100°, it melts at 153—154.5°.

[With PAKIS.]—*Ethylic piperidyl- $\alpha$ -isobutyrate*,  $C_5NH_{10} \cdot CMe_2 \cdot COOEt$ , boils at 217° under 750 mm. pressure; the acid,  $C_5NH_{10} \cdot CMe_2 \cdot COOH$ , which does not solidify very readily, crystallises from hot chloroform, and melts at 160—161°.

*Ethylic piperidyl- $\alpha$ -isovalerate*,  $C_5NH_{10} \cdot CHPr^{\beta} \cdot COOEt$ , which is a thick, yellowish oil boiling at 228° under 752 mm. pressure, can only be hydrolysed by heating with barium hydroxide for 5½ hours at 170—180° under 11—13 atmospheres pressure. The acid, after purification with benzene and chloroform, melts at 152—155°; dissolves readily in alkalis, acids, water, alcohol, or hot chloroform, but is only sparingly soluble in cold benzene, acetone, or carbon bisulphide, and insoluble in ether or light petroleum. The following list gives the percentage of reaction taking place between piperidine and the ethylic salts when 4.25 grams of the base is heated for 1 hour at 100° with equivalent quantities of the different ethylic salts. The extent to which the reaction had taken place was estimated by isolating the piperidine hydrobromide and weighing it. Ethylic bromopropionate, 91.1; ethylic bromobutyrate, 88.4; ethylic bromoisobutyrate, 56.1; ethylic bromoisovalerate, 49.4; ethylic phenylbromacetate, 50.6 per cent.

[With HOLM.]—The reaction between piperidine and the bromides of  $\alpha$ -bromo-substituted fatty acids takes place with the greatest readiness. In this way, the following compounds have been prepared.  *$\alpha$ -Bromopropiopiperidide*,  $C_5NH_{10} \cdot CO \cdot CHMeBr$ , boils at 150—152° under 10 mm. pressure, and when kept for some time at a low temperature solidifies to hygroscopic, rhombic plates melting at 30°;  *$\alpha$ -bromobutyropiperidide* distils at 144—146° under 25 mm. pressure, and melts at 125—130°;  *$\alpha$ -bromoisobutyropiperidide* boils at 147—150° under 35 mm. pressure, and melts at 121.5—122.5°;  *$\alpha$ -bromoisovaleropiperidide* melts at 65°. In all four cases, the yields were practically theoretical. J. J. S.



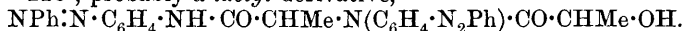
**Formation of Chains. XXX. Carbazole, Amidoazobenzene, and Acetanilide.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 2847—2854).—As an ethereal solution of carbazole, when saturated with hydrogen bromide, yields no insoluble salt, the method adopted in the case of other bases (see preceding abstract), namely, heating two molecular proportions of the base with one of an ethylic salt of a bromo-fatty acid, and determining the extent to which the reaction had taken place, by weighing the amount of hydrobromide of the base formed, could not be employed. Instead, molecular quantities of carbazole and of the ethylic salts were heated together, but no very definite results were obtained. Better results were obtained when equivalent quantities of carbazole and of bromides of different bromo-fatty acids were heated in benzene solution. 6·7 grams of carbazole was heated to boiling with 160 c.c. of benzene, and then an equivalent quantity of the acid bromide, dissolved in 40 c.c. of benzene, added during the course of an hour, the mixture being finally heated for 5 hours in a reflux apparatus. The following percentage results were obtained:  $\alpha$ -bromopropionic bromide, 87·94;  $\alpha$ -bromobutyric bromide, 84·05;  $\alpha$ -bromisobutyric bromide, 0; and  $\alpha$ -bromisovaleric bromide, 72·88. The author attempts to explain these results by his dynamical hypothesis.

[With WALDMANN.]— *$\alpha$ -Bromopropionylcarbazole*,  
 $C_{12}H_8N \cdot CO \cdot CHMeBr$ ,

purified by crystallisation from hot light petroleum and ether, melts at 125° and is readily soluble in most organic solvents with the exception of cold alcohol, ether, or light petroleum. All attempts to condense ethylic  $\alpha$ -bromobutyrate or phthalic anhydride with carbazole were fruitless.

[With KARUKOWSKI.]— *$\alpha$ -Bromobutyrylcarbazole* melts at 110°;  *$\alpha$ -bromisovalerylcarbazole* crystallises from alcohol in glistening needles melting at 130°.

[With HUREWITSCH.]—The reaction between paramidoazobenzene and the bromides of different bromo-fatty acids has been studied in the usual manner, using two molecules of the base to one of the bromide. *Paramidoazobenzene hydrobromide* crystallises from boiling water in violet-black, glistening crystals, melts at 206—207°, and is very sparingly soluble in ether, alcohol, or benzene.  *$\alpha$ -Bromopropion-amidoazobenzene*,  $NPh \cdot N \cdot C_6H_4 \cdot NH \cdot CO \cdot CHMeBr$ , forms reddish-yellow, hair-like crystals, melts at 185°, and when heated with alcoholic potash yields a small amount of a compound melting at 227—228°, probably a *lactyl* derivative,



[With KAISERSTEIN.]— *$\alpha$ -Bromobutyramidoazobenzene* crystallises from benzene in yellowish-red needles melting at 158°; when heated on platinum foil, it gives violet fumes, and with alcoholic potash gives a pale-yellow, crystalline compound melting at 280°, and probably having a constitution analogous to that of the *lactyl* derivative mentioned above.

[With SOBOLEWSKI.]—The yield of  *$\alpha$ -bromisobutyramidoazobenzene* is about 54 per cent.; it crystallises from hot benzene in orange-red needles, melts at 167—168°, and, when treated with alcoholic potash,

yields *α*-hydroxyisobutyramidoazobenzene melting at 193°. *α*-Bromoisovaleramidoazobenzene crystallises from dilute alcohol in orange-coloured needles melting at 190°.

Acetanilide (9 grams), benzene (150 c.c.), and *α*-bromopropionic bromide yield a small quantity of acetanilide hydrobromide melting at 152·5—153·5° and *α*-bromopropionanilide (compare Abstr., 1893, i, 51), the latter being probably formed by the hydrolysis of the primary condensation product. The other bromides react with acetanilide in a similar manner.

J. J. S.

**Formation of Indigo by Industrial Processes: Diastasic Functions of Indigo-yielding Plants.** By L. BRÉAUDAT (*Compt. rend.*, 1898, 127, 769—771).—The author's experiments indicate that micro-organisms play no part in the indigotic fermentation of the leaves of *Isatis alpina*. This plant, like *Indigofera anil* and other indigo-yielding species, contains a hydrolytic diastase and an oxydase; in the presence of water, the former hydrolyses indican into indigo-white and indiglucin, whilst the latter, especially in alkaline solutions, oxidises the former compound into indigotin. *Indigofera dosna*, which yields no indigo, contains neither indican nor oxydase.

G. T. M.

**Action of Chloracetone on Quinoline and Allied Bases.** By ERNST SCHMIDT and WILHELM GOEHLICH (*Arch. Pharm.*, 1898, 236, 635—640).—*Quinolylacetonyl chloride*,  $C_9H_7NCl \cdot CH_2 \cdot COMe$ , was obtained by heating a mixture of quinoline and monochloracetone in molecular proportion; it yields a *platinochloride*, as a light brown, amorphous precipitate melting with decomposition at 224—226°; and an *aurichloride* crystallising from water containing hydrogen chloride, in golden yellow needles melting at 164—165°.

Only tetrahydroquinoline hydrochloride results from the interaction of monochloracetone and tetrahydroquinoline; with methylquinoline, a similar action takes place, but a small amount of *methylquinolylacetonyl chloride* is also produced; its *platinochloride* crystallises in plates melting at 230°.

Isoquinoline reacts readily with monochloracetone, giving rise to *isoquinolylacetonyl chloride*, which crystallises from alcohol, and yields a *platinochloride* crystallising in yellowish-red needles melting at 221—223°, and an *aurichloride* as yellow, glistening needles, melting at 141°.

Codeine does not react with monochloracetone in a similar manner.

A. W. C.

**Pyrazole from Acetylene and Diazomethane.** By HANS VON PECHMANN (*Ber.*, 1898, 31, 2950—2951).—Acetylene, purified by washing with lead acetate solution and dried with sulphuric acid and calcium chloride, is passed into a stoppered flask containing an ethereal solution of diazomethane and surrounded by ice; the flask is occasionally shaken, and at the end of two days, although the yellow colour of the diazomethane has not entirely disappeared, a yield of 50

per cent. of pyrazole,  $\begin{array}{c} CH \cdot NH \\ | \quad | \\ CH \cdot CH \end{array} \gg N$ , is obtained when the ethereal solution is evaporated.

J. J. S.

**Isomeric Chlorophenyldimethyl Pyrazoles.** By AUGUST MICHAELIS and HANS RÖHMER (*Ber.*, 1899, 31, 3193—3195).—When 1-phenyl-3:4-dimethyl-5-pyrazole is heated at 150—160° with 1½ molecular proportions of phosphorus oxychloride in a closed tube, and the product purified by treatment with water, extraction with ether, and distillation under diminished pressure, 5-chloro-1-phenyl-3:4-dimethyl-

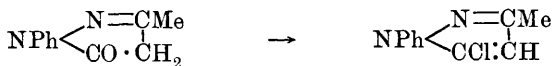
pyrazole,  $\begin{matrix} \text{CMe}=\text{N} \\ \text{CMe}:\text{CCl} \end{matrix} > \text{NPh}$ , is obtained; it is a feeble base, boils at 147° under a pressure of 12 mm., and dissolves in strong hydrochloric acid, but is reprecipitated on the addition of water; when reduced with sodium and alcohol, it yields a pyrazoline, which gives a very stable red coloration with sulphuric acid and potassium dichromate.

When antipyrine is heated with phosphorus oxychloride at 160° for 12 hours, it yields a compound isomeric with the above substance, which the authors term *antipyrinechloropyrazole*,  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{Cl}$ ; it behaves towards hydrochloric acid in the same way, but when reduced and treated with potassium dichromate and sulphuric acid, it gives a red coloration which quickly disappears. It appears to combine with 4 atoms of bromine, yielding a compound which melts at 130°; the latter is decomposed by warm soda, giving a crystalline substance which contains 1 bromine and 1 chlorine atom, and separates from dilute alcohol in very long needles melting at 52—53°.

A second product of the action of phosphorus oxychloride on antipyrine is a substance which is not extracted when the aqueous liquid is shaken with ether, but can be isolated by adding soda, evaporating to dryness, and extracting the residue with absolute alcohol, when the latter, on evaporation, deposits a considerable quantity of the substance, in the form of colourless, shining crystals, which do not give the reactions of antipyrine.

A. L.

**A Simple Conversion of Pyrazolones into Pyrazoles.** By AUGUST MICHAELIS and HANS RÖHMER (*Ber.*, 1898, 31, 2907—2908. Compare Abstr., 1891, 1068).—When 1-phenyl-3-methyl-5-pyrazolone (1 mol.) is heated with phosphorus oxychloride (1½ mols.) for 10 hours at 150°, 5-chloro-1-phenyl-3-methylpyrazole is formed, the yield being almost quantitative.



This substance boils at 142° under 9 mm. pressure.

C. F. B.

**3-Hydroxy-1-phenyl-5-pyrazolone.** By AUGUST MICHAELIS and HANS RÖHMER (*Ber.*, 1898, 31, 3003—3014).—The substance described as 1-phenyl-3:5-pyrazolidone (Abstr., 1892, 1004) appears to be, in reality, 3-hydroxy-1-phenyl-5-pyrazolone,  $\begin{matrix} \text{NPh} \cdot \text{CO} \\ \text{N}:\text{C}(\text{OH}) \end{matrix} > \text{CH}_2$ , for this constitution is most in harmony with the reactions described in the present paper. It is best obtained by allowing ethylic chloromalonate (30 grams, = 1 mol.) to remain with phenylhydrazine (3 mols.) for 3 days in a flask fitted with a Bunsen valve, dissolving the product in caustic

soda solution, extracting the solution carefully with ether several times, and then treating it with excess of hydrochloric acid, keeping it cool meanwhile. When (1 mol.) heated with phosphorus oxychloride (1 mol.) at  $100^{\circ}$  for 12 hours, it is converted into 3-chloro-

1-phenyl-5-pyrazolone,  $\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ | \\ \text{N}=\text{CCl} \end{smallmatrix} > \text{CH}_2$ , which melts at  $143\text{--}144^{\circ}$ ; with

benzaldehyde and with nitrous acid, it yields a 4-benzylidine and a 4-isonitroso-derivative respectively; these are both red, and melt at  $108\text{--}109^{\circ}$  and  $146\text{--}147^{\circ}$ ; the latter crystallises with  $2\text{H}_2\text{O}$ . When it is heated with 2 mols. of phosphorus oxychloride at  $150^{\circ}$  for 6 hours,

the product is 3:5-dichloro-1-phenylpyrazole,  $\begin{smallmatrix} \text{NPh}\cdot\text{CCl} \\ | \\ \text{N}=\text{CCl} \end{smallmatrix} > \text{CH}$ ; this

melts at  $25\text{--}26^{\circ}$  and boils at  $170\text{--}172^{\circ}$  under a pressure of 16 mm.

When 3-hydroxy-1-phenyl-5-pyrazolone is dissolved in caustic potash solution and treated gradually with methylic iodide, the solution being cooled meanwhile, 3-methoxy-1-phenyl-4-dimethyl-5-pyrazolone,

$\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ | \\ \text{N}:\text{C}(\text{OMe}) \end{smallmatrix} > \text{CMe}_2$ , is formed; this melts at  $70^{\circ}$  and boils at about

$310^{\circ}$ ; when it is dissolved in caustic soda solution and hydrochloric

acid added, a product  $\left[ \begin{smallmatrix} \text{NPh}\cdot\text{C}(\text{OH})_2 \\ | \\ \text{N}=\text{C}(\text{OMe}) \end{smallmatrix} > \text{CMe}_2 \right]$  is precipitated which

melts at  $178^{\circ}$  and contains  $1\text{H}_2\text{O}$  more than the original compound.

When the methoxydimethyl compound (1 mol.) is heated with phosphoric chloride ( $1\frac{1}{2}$  mols.) at  $120\text{--}125^{\circ}$ , methylic chloride is

evolved and a chlorophenyl dimethylpyrazolone,  $\begin{smallmatrix} \text{NPh}\cdot\text{CCl} \\ | \\ \text{N}:\text{C}(\text{OMe}) \end{smallmatrix} > \text{CMe}$ , is

formed; this melts at  $108\text{--}109^{\circ}$  and boils at  $150\text{--}160^{\circ}$  under a pressure of 22 mm.; when crystallised from water, it unites with  $1\text{H}_2\text{O}$ ,

forming a compound which melts at  $173\text{--}174^{\circ}$ . When the methoxydimethyl compound (1 mol.) is heated with phosphorus oxychloride ( $1\frac{1}{2}$  mols.) at  $150^{\circ}$  for 10 hours, it yields an isomeric chlorophenyl-

dimethylpyrazolone,  $\begin{smallmatrix} \text{NPh}\cdot\text{CO} \\ | \\ \text{N}=\text{CCl} \end{smallmatrix} > \text{CMe}_2$ , boiling at  $170\text{--}172^{\circ}$  under 22

mm. pressure, and less soluble in water than its isomeride; phosphorus oxychloride has no further action on this compound, but phosphoric chloride at  $150^{\circ}$  converts it into 3:5-dichloro-1-phenyl-4-methylpyrazole,

$\begin{smallmatrix} \text{NPh}\cdot\text{CCl} \\ | \\ \text{N}=\text{CCl} \end{smallmatrix} > \text{CMe}$ , which boils at about  $155^{\circ}$  under a pressure of

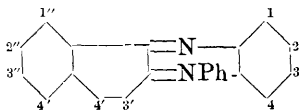
16 mm.

C. F. B.

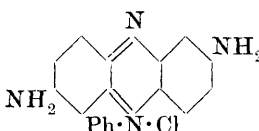
**Action of Formaldehyde on Amarine.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], 17, 864—865).—On adding formaldehyde to an alcoholic solution of amarine, the additive compound,  $\text{C}_{21}\text{H}_{18}\text{N}_2\cdot\text{CH}_2\text{O}$ , is obtained in white needles which melt at  $145^{\circ}$ ; like amarine itself, the compound is monobasic. The whole of the formaldehyde is removed on heating at  $180^{\circ}$ , and by treatment with aqueous ammonia at  $100^{\circ}$ , it is converted quantitatively into hexamethylenetetramine.

T. M. L.

**Nitro- and Amido-rosindulines.** By FRIEDRICH KEHRMANN, FERD. RADEMACHER, and OTTO FEDER (*Ber.*, 1898, 31, 3076—3087).—The influence of the introduction of amido-groups into different positions in the rosinduline molecule



on the tinctorial properties of the dyes thus formed has been studied. The introduction of an amido-group into the para-position (2) with respect to azonium nitrogen gives a bluish-violet dye which does not fluoresce. The introduction of amido-groups into the phenyl group directly attached to azonium nitrogen alters the colour of the dyes very little, and the introduction of an amido-group in the para-position (4') with respect to azine nitrogen, for example, as in the previously described naphthaphenosafranin, changes the colour slightly from red towards violet, it further increases the intensity of the colour and also the fluorescence. A similar difference is observed between naphthaphenosafranin and Nietzki-Otto's isorosinduline. Analogous differences may be observed in the safranines of the benzene series, so that it is safe to predict that the hitherto unknown

isomeride of phenosafranin, namely, , is a

violet to blue dye.

2-Nitrorosinduline chloride (compare Abstr., 1898, i, 155), when treated with sodium carbonate, yields the free base in the form of the *anhydride*,  $\text{NH} \left\langle \begin{smallmatrix} \text{C}_{11}\text{H}_5 \cdot \text{N} \\ \text{NPh} \end{smallmatrix} \right\rangle \text{C}_6\text{H}_3 \cdot \text{NO}_2$ ; this is a dark, brownish-red precipitate decomposing at about  $242^\circ$ . The *platinochloride*,

$\text{C}_{22}\text{H}_{15}\text{N}_4\text{O}_2\text{PtCl}_6$ , forms ruby-red plates with a golden lustre, and is practically insoluble in water. The *acetyl* derivative,  $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_3$ , crystallises from a mixture of alcohol and benzene in reddish-brown needles, insoluble in water; its salts with mineral acids are somewhat yellower than those of the nitrorosindulines. The *dichromate*, *nitrate*, *iodide*, and *mercurichloride* derivatives are red, crystalline compounds almost insoluble in water.

2-Amidorosinduline chloride or 2:4'-diamidophenyl naphthaphenazonium chloride, obtained when the nitro-chloride is suspended in warm alcohol and reduced with tin and hydrochloric acid, crystallises in dark violet needles with a coppery lustre; to obtain it quite pure, it is dissolved in a little boiling water and a few drops of hydrochloric acid are added to the solution. It dissolves readily in water with a blue-violet, and in alcohol with a pure blue coloration. With acids, it forms three series of salts. Dissolved in concentrated sulphuric acid, it gives a *tri-acid* salt in the form of a green solution; when this is diluted with water, the colour changes to reddish-yellow, owing to the

formation of a *di-acid* salt, and when poured into much water or when the excess of acid is neutralised, a violet *mon-acid* salt is formed. The *platinochloride*,  $(C_{22}H_{17}N_4Cl)_2PtCl_4$ , is a dark blue, crystalline powder.

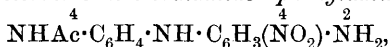
2-Acetamido-4'-amidophenylnaphthaphenazonium chloride, obtained by the action of acetic anhydride on the diamido-compound at ordinary temperatures, crystallises in small, brown needles and shows the same colour reactions as rosinduline, thus indicating that it is the amido-group in position 2, and not in position 4', which has been acetylated.

2:4'-Diacetamidophenylnaphthaphenazonium chloride, obtained by heating the diamido-compound or its monacetyl derivative with acetic anhydride and sodium acetate, crystallises in minute plates, with a yellow, metallic lustre. Its hot aqueous or alcoholic solution has a bright red colour and brick-red fluorescence. The *base* itself,  $C_{26}H_{20}N_4O_2$ , is obtained in the form of violet needles when the chloride is treated with sodium carbonate.

Paramitro-4'-amidophenylnaphthaphenazonium chloride is obtained when 3 grams of Nietzki and Baum's nitramidodiphenylamine (Abstr., 1896, i, 164) is suspended together with 2.2 grams of oxynaphthaquinonimide in 50 c.c. of alcohol containing 0.8 gram of hydrochloric acid (20 per cent.), and the mixture kept at the ordinary temperature during 3 months; the corresponding rosindone is formed at the same time, and may be removed by repeated extraction with hot benzene. The chloride resembles rosinduline chloride, but is somewhat yellower, and more sparingly soluble in water. The *base* itself crystallises in reddish-yellow needles decomposing at  $260^\circ$ .

4'-Paradiamidophenylnaphthaphenazonium chloride,  $C_{22}H_{17}N_4Cl + 2H_2O$ , crystallises in metallic-green prisms and is readily soluble in water; its aqueous and alcoholic solutions have a blood-red colour and a slight red fluorescence. The free *base* is readily transformed into the carbonate when left exposed to the air.

Paracetamidodinitrodiphenylamine, when reduced with ammonium sulphide, yields acetamidonitro-orthamidodiphenylamine,



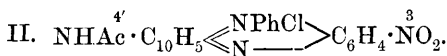
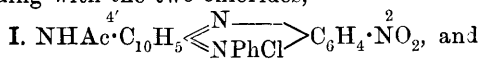
which crystallises from alcohol in golden, glistening scales, melting at  $254-255^\circ$ ; this, when condensed with oxynaphthaquinonimide by the aid of hydrochloric acid, yields 2-nitro-4'-paradiamidophenylnaphthaphenazonium chloride,  $C_{22}H_{16}N_5O_2Cl + 3H_2O$ , which crystallises from alcohol in brick-red plates with a golden lustre; it is fairly readily soluble in water and alcohol, and yields a *monacetyl* derivative crystallising in dark red needles. The free *base* from this acetyl derivative sinters at  $250^\circ$ . The *diacetyl* derivative,  $C_{26}H_{20}N_5O_4Cl$ , forms light red crystals, and yields a violet-red base which sinters at  $260-261^\circ$ .

2:4'-Paratriamidophenylnaphthaphenazonium chloride crystallises in long, glistening, black-violet needles soluble in alcohol or water. The *base* forms violet-blue needles and appears to yield four series of salts.

J. J. S.

Nitro- and Amido-derivatives of Phenylisonaphthaphenazonium and of Methylnaphthaphenazonium. By FRIEDRICH KEHRMANN and HENRI JACOB (Ber., 1898, 31, 3087-3097).—Hydroxynaphthaquinonimide reacts with nitrophenylorthophenylene-

diamine, yielding rosinduline derivatives (see preceding abstract). 4-Acetamido-1 : 2-naphthaquinone reacts with an alcoholic solution of the sulphate of the same base, yielding two isomeric sulphates corresponding with the two chlorides,



The former is identical with the sulphate obtained from oxynaphthaquinonimide and nitrophenylorthophenylenediamine sulphate. The two sulphates, which are accompanied by a bye-product insoluble in water, are precipitated as the chlorides, then hydrolysed with 50 per cent. sulphuric acid, and, when cold, the sulphate corresponding to I. crystallises out. The second sulphate is converted into the chloride, and is thus obtained in the form of blackish-green crystals; it may be recrystallised from 20 per cent. hydrochloric acid, but a small quantity is always converted into an insoluble brown isomeric chloride, probably having the constitution,



This compound is more readily obtained when a more dilute acid (5—10 per cent.) is employed. The brown isomeride is practically insoluble in alcohol or water, but dissolves in hot methylic alcohol, and when hydrogen chloride is passed into this solution, the brown salt becomes reconverted into the green. The free base corresponding with this chloride has not been isolated in a pure form. 4-Acetamido-1 : 2-naphthaquinone also reacts with nitromethylorthophenylenediamine hydrochloride, yielding two isomeric rosinduline derivatives; they are somewhat difficult to separate, but the one is rather more readily hydrolysed than the other. When boiled with alcohol, they yield *nitracetamidonaphthaphenazine*, decomposing between 295° and 300°. Hydroxynaphthaquinonimide reacts with nitromethylorthophenylenediamine hydrochloride, yielding *2-nitro-4'-amidomethylnaphthaphenazonium chloride*,  $\text{C}_{17}\text{H}_{13}\text{N}_4\text{O}_2\text{Cl}$ , which crystallises from alcohol in metallic green needles, and is soluble in water or alcohol; its *platinochloride* and *aurichloride* form red, crystalline precipitates insoluble in water. When heated with sodium acetate and acetic anhydride, it yields *2-nitro-4'-acetamidonaphthaphenazine*, which crystallises from nitrobenzene in orange-yellow needles insoluble in water, but dissolving in alcohol to a yellow solution with a green fluorescence. When hydrolysed with sulphuric acid, it yields *4'-amido-2-nitromethylnaphthaphenazonium sulphate*, as a blood-red precipitate, from which, by removal of the amido-group *2-nitromethylnaphthaphenazonium* may be obtained. The *chloride*,  $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2\text{Cl}$ , of the latter compound crystallises in orange-yellow plates which are readily soluble in alcohol or hot water, the alcoholic solution exhibiting a yellow fluorescence; the *nitrate*, which is insoluble in dilute nitric acid, crystallises in glistening, golden plates. *2-Amidomethylnaphthaphenazonium chloride*,  $\text{C}_{17}\text{H}_{14}\text{N}_3\text{Cl}$ , obtained by the reduction of the nitro-compound with stannous chloride and hydro-

chloric acid, crystallises in dark violet, almost black, glistening needles, and is readily soluble in alcohol or water, but its solutions are not fluorescent. The *aurichloride*, *platinochloride*, *nitrate*, *acetyl derivative*, and *platinochloride* of the acetyl derivative have been prepared.

J. J. S.

**The Sixth Isomeride of Rosinduline.** By FRIEDRICH KEHRMANN, and ALBERT LEVY (*Ber.*, 1898, **31**, 3097—3106).—2-*Nitrophenylisonaphthaphenazonium ferrichloride*,  $C_{22}H_{14}N_3O_2FeCl_4$ , is obtained by condensing nitrophenylorthophenylenediamine sulphate with  $\beta$ -naphthaquinone and pouring the product into ferric chloride solution; it cannot be crystallised without undergoing decomposition. The *nitrate*,  $C_{22}H_{14}N_3O_2 \cdot NO_3$ , crystallises in pale red needles, and the *platinochloride*,  $(C_{22}H_{14}N_3O_2)_2PtCl_6$ , forms a yellowish-red, crystalline powder insoluble in water.

2-*Acetamidophenylisonaphthaphenazonium chloride*,  $C_{24}H_{18}N_3OCl$ , obtained when the iron double salt is reduced with stannous chloride and hydrochloric acid, and the crude product heated with acetic anhydride and sodium acetate, forms small, yellowish-red crystals and dissolves in hot water or alcohol, yielding non-fluorescent solutions. The *platinochloride* and *dichromate*,  $(C_{24}H_{18}N_3O)_2Cr_2O_7$ , are both insoluble in water.

2-*Amidophenylisonaphthaphenazonium bromide*,  $C_{22}H_{16}N_3Br$ , forms black crystals with a bronzy lustre, and is readily soluble in alcohol or water, yielding violet solutions. The *platinochloride*,  $(C_{22}H_{16}N_3)_2PtCl_6$ , crystallises in bluish-black needles. Amines readily react with the salts of this new isomeride of rosinduline, as the para-position to the azine nitrogen is free. The amine residue which is thus introduced takes the ortho-position relatively to the amido-group already present, and orthodiamines are thus obtained which can be converted into fluorindine compounds.

3-*Dimethylamido-2-amidophenylisonaphthaphenazonium nitrate*,  $C_{24}H_{21}N_4 \cdot NO_3 + H_2O$ , obtained by the action of dimethylaniline on the "tin double salt" of the isorosinduline suspended in alcohol, and by subsequent treatment with potassium nitrate, crystallises from water in green, glistening needles; it dissolves in water or alcohol, yielding magenta-coloured solutions. The *chloride*, which is readily soluble in water, and the *platinochloride* and *dichromate*, both of which are sparingly soluble, have also been prepared.

3-*Anilido-2-amidophenylisonaphthaphenazonium chloride*,  $C_{28}H_{21}N_4Cl$ , obtained by the action of aniline on the "tin double salt," forms bronzy, glistening crystals. Diethylamine reacts with the "tin double salt," yielding 2-*amidoisorosindone*,  $O \begin{array}{c} \diagup NPh \\ | \\ C_6H_3(NH_2):N \end{array} - C_{10}H_6$ , which crystallises

from alcohol or benzene in yellowish-red plates melting above  $300^\circ$ . Acetylisorosinduline chloride, when treated with dimethylamine in slight excess, yields *acetamidoisorosindone*, which, on hydrolysis with 50 per cent. sulphuric acid, yields *amidoisorosindone*, and from this, by removal of the amido-group, *isorosindone*,  $C_{22}H_{14}N_2O$ , the third and last theoretically possible isomeride of rosindone, is obtained. It crystallises from benzene in reddish-violet plates with a coppery lustre, and melts at  $267^\circ$ ; it is insoluble in water or alkalis, but



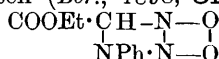
dissolves in alcohol, ether, acetic acid, or benzene, yielding violet-red solutions; the alcoholic solution exhibits a faint red fluorescence.

The green 2-nitro-4'-amidophenylisonaphthaphenazonium described in the preceding abstract may be converted into 2-amidophenylisonaphthaphenazonium (see above) by eliminating the amido-group, and then reducing the nitro-compound. The same nitramido-compound (either brown or green modification), when reduced with stannous chloride, yields 2:4'-diamidophenylisonaphthaphenazonium chloride as bronzy, lustrous crystals. It is an extremely strong base, as both amido-groups are in the para-position relatively to azonium nitrogen, and yields an insoluble *platinochloride*. J. J. S.

**Condensation Products from Flavinduline and Deoxybenzoin.** By FRANZ SACHS (*Ber.*, 1898, 31, 3073—3075).—Flavinduline (*Annalen*, 1896, 292, 266), as a type of the azonium bases, readily reacts with methylene compounds, yielding characteristic colorations. When an alcoholic solution of the azonium chloride and an equivalent quantity of any of the following compounds is treated with potassium hydroxide, even in the cold, an intense green coloration is developed; ethylic acetoacetate and its substituted derivatives, ethylic cyanacetate, ethylic malonate, malononitrile, acetylacetone, phloroglucinol, resorcinol, benzylic cyanide, and deoxybenzoin. The condensation product with deoxybenzoin has been more closely examined; a solution of 2 grams of deoxybenzoin in alcohol is added to a solution of 4.4 grams of commercial flavinduline (containing 13 per cent. of ash) in 300 c.c. of alcohol, and the mixture treated with the theoretical quantity of sodium hydroxide solution, and heated to the boiling point of the alcohol. When quickly cooled and allowed to remain for 24 hours, dark coloured crystals of a compound,  $C_{40}H_{28}N_2O_2$ , similar in appearance to potassium permanganate, are obtained; this is insoluble in water or light petroleum, sparingly soluble in alcohol, more readily in acetone, ether, or ethylic acetate, and readily in toluene, benzene, chloroform, carbon tetrachloride, carbon bisulphide, or methylal. Most of its solutions are green or bluish-green; its alcoholic solution, when treated with a few drops of hydrochloric acid, yields an intense blue solution of a salt, but when this solution is boiled, it changes to an orange-red colour; the latter can also be obtained by passing dry hydrogen chloride into a solution of the base in toluene. Apparently, two isomeric salts exist in the two coloured solutions. The orange-red salt yields a *platinochloride*,  $(C_{40}H_{27}N_2O_2)PtCl_6$ . It is probable that the two different colours are due to the presence of two different chromophore groups of the ortho- and para-quinone types.

J. J. S.

**Compounds containing a previously unknown Ring.** By MILORAD Z. JOVITSCHITSCH (*Ber.*, 1898, 31, 3036).—The compound,



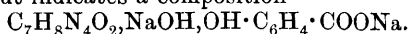
(*Abstr.*, 1898, i, 93), has the normal molecular weight. The product of hydrolysis is most likely a mixture.

M. O. F.

**Products of the Action of Sulphur on Dimethylaniline.** By RICHARD MÖHLAU and VOLKMAR KLOPPER (*Ber.*, 1898, **31**, 3164—3166. Compare Abstr., 1888, 364)—The compound  $C_8H_7NS_2$ , which was previously found to be the primary product of the action of sulphur on dimethylaniline, melts at  $88-89^\circ$ , boils at  $335^\circ$ , and yields a *platinochloride*,  $(C_8H_7NS_2)_2 \cdot H_2PtCl_6$ , which crystallises in yellowish-red prisms. It is not attacked by hydriodic acid, but is converted by nitric acid into *iso- $\mu$ -methylbenzothiazole*,  $CH_2 \begin{smallmatrix} N-C_6H_4 \\ | \\ S-CH \end{smallmatrix} S$ , which crystallises in compact plates, melts at  $202^\circ$ , and yields a *platinochloride* crystallising in yellow tablets. The base, when heated with sulphur, is converted into benzothiazole. All these reactions point to the formula  $\begin{smallmatrix} CH_2 \cdot N-C_6H_4 \\ | \\ S-CH \cdot S \end{smallmatrix}$  as the most probable for the original compound.

A. H.

**Composition of Diuretin.** By ABA VON SZTANKAY (*Chem. Centr.*, 1898, i, 1281—1282; from *Pharm. Post.*, **31**, 189—190 and 201—202).—Diuretin is said to be a double compound of the sodium compound of theobromine with sodium salicylate; it is a homogeneous substance, for it can be precipitated unchanged by means of alcohol. The unpleasant effects caused by a dose of diuretin led the author to suspect that the sodium theobromine compound is not a simple derivative of dimethylxanthine, obtained by replacing the hydrogen atom by an atom of sodium, and the analysis of the compound prepared by the action of sodium ethoxide on theobromine corresponded with a composition  $C_7H_8N_4O_2 \cdot NaOH$ . Moreover, in three experiments, from 1.3 grams of theobromine, 0.23 of sodium, and 1.6 of anhydrous sodium salicylate, 3.807, 3.807, and 3.806 grams of diuretin were obtained respectively. This increase of weight, according to the author, cannot be ascribed to any hygroscopic character of the substance, but indicates a composition



E. W. W.

**Active Principles of Certain Aroids.** By ALEXANDRE HÉBERT and F. HEIM (*Bull. Soc. Chim.*, 1898, [iii], **17**, 664—669).—Examinations of extracts obtained from *Arum maculatum* and *A. italicum*, *Arisarum vulgare*, *Amorphophallus Rivieri*, and *Caladium bulbosum* have demonstrated the presence of an acid saponine and a volatile, liquid alkaloid; the latter was obtained as a brown, unstable liquid, having a sharp taste and an odour of mice; it is sparingly soluble in water, but dissolves in alcohol, benzene, amylic alcohol, chloroform, ether, and petroleum, fumes in presence of hydrogen chloride and gives a hydrochloride which is soluble in alcohol. The properties of the base closely resemble those of coniine, but its toxic power is apparently more feeble than in the case of that alkaloid. No appreciable quantity of hydrogen cyanide could be obtained from any portion of the above aroids.

A. I.

## Organic Chemistry.

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**Action of Acetylene on Metal Ammoniums.** By HENRI MOISSAN (*Compt. rend.*, 1898, 127, 911—917).—When ammonia is liquefied in contact with sodium, potassium, lithium, and calcium, and acetylene is passed into the liquid, cooled at  $-40^{\circ}$  to  $-80^{\circ}$ , the deep blue colour gradually disappears, and a colourless liquid is obtained, ethylene being liberated when the temperature is allowed to rise. When the colourless liquid is strongly cooled, or when the ammonia is allowed to volatilise, a white, crystalline solid is obtained. Sodium yields the compound  $C_2HNa$  in microscopic, rhombohedral lamellæ. The author considers that it is more accurately represented by the formula  $C_2Na_2, C_2H_2$ ; if it is suspended in benzene, and iodine is added until a permanent coloration is obtained, the insoluble residue consists of the carbide  $C_2Na_2$ , and contains no sodium iodide, whilst the benzene contains carbon iodide. Potassium yields the analogous compound  $C_2K_2, C_2H_2$ , which crystallises readily in brilliant, silky, rhombohedral lamellæ.

Lithium yields rhombohedra of the compound  $C_2Li_2, C_2H_2, 2NH_3$ , which becomes incandescent in contact with water or when thrown into chlorine; it also takes fire in contact with carbonic anhydride or sulphurous anhydride.

Calcium yields transparent prisms of the compound  $C_2Ca, C_2H_2, 4NH_3$ , which also becomes incandescent in contact with water, chlorine, carbonic anhydride, or sulphurous anhydride.

All these compounds dissociate when heated, and yield the carbides  $C_2Na_2$ ,  $C_2K_2$ ,  $C_2Li_2$ , and  $C_2Ca$  respectively. C. H. B.

**Action of Chlorine on Acetylenic Tetrabromide in the Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1897, [iii], 17, 799—801).—When a mixture of acetylenic tetrabromide (100 grams) with anhydrous aluminium chloride (30 grams) is heated at  $70^{\circ}$ — $80^{\circ}$  in a reflux apparatus, there is a slow, but distinct, liberation of hydrogen chloride, and on passing chlorine into the mixture, much hydrogen chloride and large quantities of bromine are evolved. From the solid product of the reaction, hexachlorethane was isolated. The same compound is formed by the action of chlorine on ethylenic bromide in the presence of aluminium chloride.

N. L.

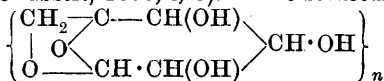
**Action of Chlorine on Pentachlorethane in Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1897, [iii], 17, 797—799).—No reaction occurs when chlorine is passed into pentachlorethane, heated at  $70^{\circ}$  in a reflux apparatus and exposed to diffused light, but on adding aluminium chloride, the gas is completely absorbed, there is an abundant evolution of hydrogen chloride, and hexachlorethane is formed in almost theoretical quantity. When pentachlorethane is heated at  $70^{\circ}$  with aluminium chloride alone, there is a decided evolution of hydrogen chloride, together with the forma-

tion, it is suggested, of a compound of the formula  $\text{CCl}_3 \cdot \text{CCl}_2 \cdot \text{AlCl}_2$ , which is converted by the action of chlorine into hexachlorethane, with regeneration of aluminium chloride. N. L.

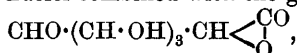
**The Sugar of Diabetic Urine.** By LE GOFF (*Compt. rend.*, 1898, 127, 817—819).—The sugar was isolated in a pure state by evaporating the urine in a vacuum, separating the crystals formed by filtration, washing with cold alcohol of  $90^\circ$  in order to remove urea, colouring matter, and chlorides, and finally crystallising several times from boiling alcohol of  $95^\circ$ . The crystals thus obtained had the composition  $\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O}$ , but on standing lost the greater part of their water of crystallisation; the sugar was easily fermented by yeast, reduced Fehling's solution, and had  $[\alpha]_D = 49.46$  when dissolved as  $\text{C}_6\text{H}_{12}\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}$ . Its osazone melted at  $230^\circ$ ; *d*-glucosazone, according to G. Bertrand, melts at the same temperature, and not at  $204$ — $205^\circ$  as stated by Fischer. On oxidation, the sugar gave rise to *d*-gluconic acid, which was characterised by the rotatory power of its calcium salt; from this and the foregoing properties, the sugar isolated appears to be identical with *d*-glucose, a result which is in accord with the views generally held. W. A. D.

**Action of Potash on Oxynitrocellulose.** By LÉO VIGNON (*Compt. rend.*, 1898, 127, 872—874).—Oxynitrocellulose, prepared by the method previously described by the author (*Abstr.*, 1898, i, 8), dissolves in aqueous caustic potash (sp. gr. = 1.162) with considerable development of heat, giving a brown solution; little gas is evolved. On neutralising the product with acetic acid at  $0^\circ$ , and subsequently passing hydrogen sulphide during 2 hours at the ordinary temperature, oxides of nitrogen are evolved and sulphur deposited; after warming on the water-bath to expel dissolved gases, and subsequently cooling, 20 c.c. of a solution containing 12 grams of phenylhydrazine and 7.5 grams of glacial acetic acid in 100 c.c. of water is added, when a crystalline precipitate separates, especially if the solution is warmed at  $80^\circ$  for 20 minutes; on recrystallising the product from toluene, light yellow prisms are obtained which melt and decompose at  $204^\circ$ , and probably consist of the osazone of Will's hydroxypyruvic acid,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{COOH}$ , obtained by acting with potash on collodion (*Abstr.*, 1891, 542, and 1892, 356).

If a  $\text{C}_6$ -formula be assumed, oxycellulose, from its properties, appears to be a trihydric alcohol, possessing certain aldehydic and acid functions (compare *Abstr.*, 1898, i, 8). The structure



is provisionally assigned to cellulose, whilst the oxycelluloses appear to contain *n* cellulose nuclei combined with the group



characteristic of oxycellulose; on hydration, the latter group is transformed into the acid  $\text{CHO} \cdot (\text{CH} \cdot \text{OH})_4 \cdot \text{COOH}$ , which is capable of undergoing further change in two different ways according to the

equations (1)  $C_6H_{10}O_7 = CO_2 + 3H_2O + C_5H_4O_2$ , furfuraldehyde being formed, or (2)  $C_6H_{10}O_7 + O_2 = 2C_3H_4O_4 + H_2O$ , in which case hydroxypyruvic acid is produced. The formation of the latter from oxynitrocellulose is thus explained if it be assumed that the  $NO_3$  groups present serve as a means of supplying the oxygen required by the second of the above equations.

W. A. D.

**Action of Hydrocyanic Acid on Epichlorhydrin.** By ROBERT LESPIEAU (*Compt. rend.*, 1898, 127, 965—966).—When 150 grams of epichlorhydrin are heated with 70 grams of pure hydrogen cyanide in a sealed tube at  $60^\circ$  for 60 hours, a yellowish liquid is obtained which has the composition  $C_4H_6ClON$ , and boils at  $110$ — $111^\circ$  under a pressure of 2 mm., and at about  $140^\circ$  under a pressure of 15 to 20 mm. When dissolved in ethylic alcohol and heated with hydrogen chloride, it yields an ethereal salt,  $C_6H_{11}ClO_3$ , which boils at  $121$ — $122^\circ$  under a pressure of 14 mm.

The nitrile probably has the constitution  $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot CN$ .  
C. H. B.

**Non-explosive Decomposition, and Determination of the Stability of Gun-cotton.** By C. HOITSEMA (*Zeit. physikal. Chem.*, 1898, 27, 567—578).—The author has previously shown that, with some compounds, rapid and slow decomposition yield identical products, whilst for others the reverse obtains (*Abstr.*, 1897, ii, 17); gun-cotton belongs to the latter class, so that no explosion-velocity experiments are possible. At about  $150^\circ$ , it can be slowly decomposed without explosion, evolving gases containing a little nitric peroxide, and leaving a non-explosive, peat-like mass containing about 7 per cent. of nitrogen. The formation of higher oxides of nitrogen does not appear to be due to secondary reactions, as, by means of apparatus described, it is proved to precede the formation of nitric oxide. It seems more probable, therefore, that the higher oxides are due to impurity, or are produced merely in the initial stages of the reaction. The usual method for the determination of the stability of gun-cotton is the observation of the time which elapses before nitric fumes are evolved when the sample is kept at a certain fixed temperature. In the apparatus described, the explosive may be maintained for any length of time at any desired temperature, and the author considers a better method of determining the stability to consist in ascertaining the highest temperature at which the sample may be kept for a quarter of an hour, or some such time, without the production of nitric fumes.

L. M. J.

**Action of Oxidising Agents on Nitrogenous Compounds.** By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, 127, 1028—1030. Compare *Abstr.*, 1898, i, 548, 564, and 566).—The author has investigated the action of concentrated solutions of chromic acid and potassium dichromate on solutions of amines and amides. Hydroxylamine is at once decomposed with the evolution of nitrogen and nitrous fumes. Phenylhydrazine and methylphenylhydrazine yield nitrogen, and, when the action is aided by heat, a small amount of phenol is produced. Urethane is attacked by warm chromic acid, but is not affected by dichromate. Acetamide is only partially de-

composed by warm chromic acid, but if warmed with an alkaline solution of potassium chromate, a considerable quantity of nitrogen is evolved; benzamide under these conditions is scarcely affected. Carbamide is oxidised by warm solutions of the above reagents, but less energetically than by alkali hypochlorites. Thiocarbamide is very stable towards these agents; the decomposition is partial, and a mixture of carbonic anhydride and nitrogen in molecular proportion is evolved. Phenylthiocarbamide is not attacked by dichromate, but is oxidised by chromic acid, carbonic anhydride (1 mol.) being liberated. The hydrochlorides of methylamine and ethylamine are decomposed, giving rise to chlorine, nitrogen, and carbonic anhydride, together with a small quantity of free oxygen (see next abstract). G. T. M.

**Action of Oxidising Agents on Fatty and Aromatic Amines.** By WILLIAM OECHSNER DE CONINCK and A. COMBE (*Compt. rend.*, 1898, 127, 1221—1223).—When strong, aqueous solutions of chromic acid in potassium dichromate are warmed with the hydrochlorides of methylamine and ethylamine, very little action takes place; in presence of a little dilute sulphuric acid, however, gradual decomposition occurs, and carbonic anhydride, chlorine, and nitrogen are evolved. Even ammonium chloride is decomposed by a very strong solution of the oxidising mixture.

The hydrochlorides of aniline, ortho- and para-toluidines, diphenylamine, the phenylenediamines and rosaniline yield large quantities of carbonic anhydride, and aromatic amines in general yield colouring matters in addition. Benzylamine gives carbonic anhydride and a notable quantity of benzaldehyde. Piperidine is slowly attacked by the warm mixture, being more stable than the aromatic amines in this respect. A. L.

**Salts of Perchromic Acid.** By O. FRITZ WIEDE (*Ber.*, 1898, 31, 3139—3143. Compare Abstr., 1898, ii, 28, 295).—These salts were obtained by adding a small quantity of the base to an ethereal solution of perchromic acid cooled below 0°, and drying the crystals on a porous plate; the tetramethylammonium hydroxide had to be added in aqueous solution, of course, but the water was removed from the mixture in the form of ice; in the preparation of the quinoline compound, the ethereal solution of perchromic acid was diluted with an equal volume of light petroleum, when the water dissolved in the ether solidified. None of the compounds now described crystallised with a molecule of hydrogen peroxide.

*Tetramethylammonium perchromate*,  $\text{CrO}_5\text{NMe}_4$ , forms a brownish-violet, crystalline powder; in the cold, it loses oxygen slowly, leaving the dichromate; when it is heated, oxygen is first evolved with a hissing noise, and then the yellow dichromate left burns, sending out a shower of sparks. When the salt is mixed with solutions of silver nitrate or barium chloride, the oxides of these metals are formed, from which it may be inferred that their perchromates are incapable of existence.

*Trimethylammonium perchromate* is dark-coloured; it is spontaneously explosive, unlike either the ammonium or tetramethylammon-

ium salt. *Quinoline perchromate*,  $\text{CrO}_5\text{H}_7\text{NC}_9\text{H}_7$ , is blue and unstable; it explodes slightly when heated. *Piperidine perchromate*,  $\text{CrO}_5\text{H}_7\text{NC}_5\text{H}_{11}$ , is dark violet in colour, and very soluble in water; it explodes when heated.

C. F. B.

**Active Methylbutylenediamine (2-Methyl-1:4-diaminobutane).** By L. ETAIX and PAUL FREUNDLER (*Bull. Soc. Chim.*, 1897, [iii], 17, 805—808).—The ethereal salts of  $\beta$ -methyladipic acid form an exception to the law of the product of asymmetry, and it therefore seemed of interest to ascertain whether a reduction in the length of the chains attached to the asymmetric carbon atom would be accompanied by an increase in the rotatory power, a change the reverse of that which occurs when the attached groups are lengthened. For this purpose, ethylic  $\beta$ -methyladipate was converted into methylbutylenediamine through the hydrazide and azide, according to Curtius' method. The ethylic salt employed had a rotatory power  $[\alpha]_D = +3^\circ$ , and was prepared from the menthone obtained by the action of dilute sulphuric acid on menthol.

$\beta$ -Methyladipic hydrazide,  $\text{N}_2\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_2\text{H}_3$ , obtained by heating a mixture of ethylic  $\beta$ -methyladipate (75 grams) with fuming hydrazine hydrate (55 grams) for 6 hours at  $150$ — $170^\circ$ , crystallises in colourless needles melting at  $136^\circ$ , and is soluble in water, boiling alcohol, and acetone, but almost insoluble in cold alcohol and in other organic solvents.  $\beta$ -Methyladipic azide,  $\text{C}_5\text{H}_7(\text{CO}\cdot\text{N}_3)_2$ , prepared by adding sodium nitrite (3 mols.) to a solution of the hydrazide in 10 times its weight of water at  $0^\circ$ , is a heavy, brownish oil which does not solidify at  $-10^\circ$ ; it cannot be completely purified, owing to its rapid decomposition at the ordinary temperature. The azide is heated for some time with absolute alcohol in a reflux apparatus, and the mixture of the urethane with the corresponding carbamic acid which is thus obtained is heated in sealed tubes at  $130$ — $150^\circ$  with concentrated hydrochloric acid; the contents of the tubes are then filtered, saturated with solid caustic potash, and the methylbutylenediamine extracted with ether and purified by distillation.

Active methylbutylenediamine,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , is a mobile, fuming liquid of fœtid odour, boiling at  $170^\circ$ ; its specific rotatory power is  $[\alpha]_D = +30.5^\circ$ . The hydrochloride crystallises in small prisms soluble in water and alcohol; the platinochloride in orange scales melting and decomposing at  $200^\circ$ ; the picrate in small, yellow needles decomposing at about  $180^\circ$ . The dibenzoyl derivative crystallises in colourless needles melting at  $151$ — $152^\circ$ , and is soluble in alcohol, but insoluble in water.

As was anticipated, the rotatory power of methylbutylenediamine is greater than that of ethylic methyladipate. It is somewhat remarkable that the rotatory power of the latter was not destroyed by the successive operations to which it was subjected, and it is inferred that racemisation depends, not on the agents of transformation, but on the nature of the groups attached to the asymmetric carbon atom. Active substances in which these groups are hydrocarbon radicles, or are attached by means of intermediate hydrocarbon residues, appear to possess a special degree of stability.

N. L.

**Glucosamine [Chitosamine] Hydrochloride.** By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 802—805).—Glucosamine hydrochloride exhibits the phenomenon of birotation, and should, therefore, exist in two modifications. The  $\alpha$ -variety has the higher rotatory power, and is the ordinary salt obtained by crystallisation from water, whilst the more stable  $\beta$ -variety, of lower rotatory power, has hitherto been known only in solution. A number of determinations of the rotatory power of solutions of the  $\beta$ -modification, obtained by heating solutions of ordinary glucosamine hydrochloride, or by allowing them to remain for 1 or 2 days, gave  $+72.5^\circ$  as the value of  $[\alpha]_D$ , a result which is appreciably higher than those obtained by Ledderhose, Tiemann, and Hoppe-Seyler. This difference is, in all probability, due to excessive heating of the solutions employed by those observers, for it was found that the rotatory power of a 10 per cent. solution was reduced to  $70.8^\circ$  by 14 minutes heating in the water-bath, and to  $70.0^\circ$  after 28 minutes. The value of  $[\alpha]_D$  for  $\alpha$ -glucosamine hydrochloride was found to be  $+100^\circ$ , the solution being prepared and the determination made within 4 minutes at  $20^\circ$ .

$\beta$ -Glucosamine hydrochloride was obtained in the form of microscopic crystals by pouring a concentrated solution, prepared at  $60^\circ$ , into 10 times its weight of absolute alcohol. When dissolved in water and quickly examined, the rotatory power was found to be  $+75^\circ$ , but after some hours it fell to  $72.5^\circ$  owing to the re-formation of the  $\alpha$ -variety. The two modifications of glucosamine hydrochloride, specimens of which were examined by Wyrouboff, crystallise in different systems, the  $\alpha$ -variety in the monoclinic, and the  $\beta$ -variety in the hexagonal, system. N. L.

**Glucosines.** By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 801—802).—The discrepancies between the author's results and those obtained by Brandes and Stoehr (*Abstr.*, 1897, i, 230) in the examination of  $\alpha$ - and  $\beta$ -glucosine are due to essential differences in the methods by which the bases were obtained. N. L.

**Valency of Boron.** By Sir EDWARD FRANKLAND (*Compt. rend.*, 1898, 127, 798—799).—In discussing the structure of the substance  $\text{NaB}(\text{OEt})_4$ , which Copaux has adduced as the first certain proof of the pentad nature of boron (this vol., i, 183), the author points out that in ascribing formulæ to ammonia-borotrimethyl,  $\text{H}_3\text{N}:\text{BMe}_3$ , and to the substance  $\text{B}(\text{OEt})_3:\text{BEt}(\text{OEt})_2$  (*Abstr.*, 1876, 618), he also has previously assumed boron to be pentad. Both these compounds dissociate, however, when distilled, although their constituents recombine on cooling; in this respect, they resemble ammonium chloride, and consequently the objections which can be raised against the pentad nature of nitrogen are also valid in the case of boron. From the fact that ethylic iodide at  $140^\circ$  does not interact with the compound described by Copaux, the author considers that the formula  $\text{ONa}:\text{BEt}(\text{OEt})_3$  should be given to the latter, rather than that assigned to it by the discoverer. W. A. D.

**Action of Oxygen on Solutions of Formaldehyde.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], 17, 938—940).—Oxygen is without action on aqueous solutions of formaldehyde at



ordinary temperatures, but is rapidly absorbed at 200°. In presence of caustic potash, there is no absorption of oxygen at temperatures below 100°, but in the course of a month at ordinary temperatures complete transformation of the aldehyde into formate and methylic alcohol occurs; in presence of platinum sponge, however, the supernatant oxygen is slowly replaced by an equal bulk of carbonic anhydride, in accordance with the equation  $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$ , and this change goes on equally rapidly in darkness or on exposure to light. A. L.

**Action of Bromine on Chloral in the Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1897, [iii], 17, 796—797).—Two hundred and fifty grams of finely powdered anhydrous aluminium chloride was dissolved in 500 grams of chloral the liquid heated to 75—80°, and bromine gradually added until it was no longer absorbed. On pouring the mixture into dilute aqueous soda, a substance was precipitated which proved to be hexachlorethane. This compound is also the product of the action of iodine on chloral in the presence of aluminium chloride. N. L.

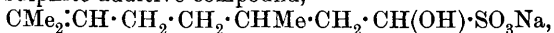
**Aliphatic Aldazine Derivatives and their Products of Rearrangement.** By ADOLF FRANKE (*J. pr. Chem.*, 1898, [ii], 58, 464).—With reference to the work of Curtius and Zinkeisen (this vol., i, 165), the author points out that he had already prepared the aldazine of isobutyraldehyde from hydrazine hydrate and isobutyraldol (*Monatsh.*, 17, 643, 672). This aldazine gives a beautifully crystalline hydrochloride, which, when treated with caustic potash, yields, not the aldazine, but an isomeric substance smelling strongly of camphor. It is probably produced by rearrangement and closing of the ring. The author proposes to further study this point. A. W. C.

**History of Citral.** By FERDINAND TIEMANN (*Ber.*, 1898, 31, 3278—3296).—The author gives a *résumé* of the more important researches on citral. J. J. S.

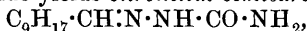
**Hydrosulphonic Acid Derivatives of Cinnamaldehyde, of Citronellal, and of Citral.** By FERDINAND TIEMANN (*Ber.*, 1898, 31, 3297—3324).—[With PAUL KRÜGER.]—Heusler's work (*Abstr.*, 1891, 1052) on the hydrosulphonic derivatives of cinnamaldehyde has been repeated, and the results confirmed. The addition of sulphurous acid to an unsaturated compound takes place more readily when a normal instead of an acid sulphite is employed, provided the alkali which is formed during the reaction is neutralised by a bicarbonate or by carbonic anhydride. When cinnamaldehyde is covered with a 20—25 per cent. solution of sodium sulphite, and carbonic anhydride is bubbled through the mixture, the whole of the aldehyde, with the exception of small quantities of impurities, goes into solution; similar results are obtained when the aldehyde (1 mol.) is shaken with a solution of sodium sulphite (2 mols.) and sodium hydrogen carbonate (2 mols.). If the aldehyde solution is then covered with ether and shaken with an excess of sodium hydroxide, 75 per cent. of the aldehyde is recovered, and on warming and again extracting with ether, a further quantity of aldehyde is obtained, but in no case more

than 80 per cent. It is thought probable that two isomeric sulphonic acids,  $\text{SO}_3\text{H}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COH}$  and  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{COH}$ , may be formed, one of which is more readily decomposed than the other.

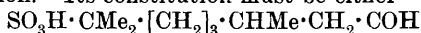
Sulphurous anhydride reacts with citronellal in a somewhat violent manner, pulegone and its hydrosulphonic acids being formed, which then yield terpenes and polyterpenes. The normal citronellal sodium hydrogen sulphite additive compound,



obtained by shaking an ice cold solution of sodium hydrogen sulphite (free from anhydride) with the aldehyde, is readily soluble in water, but may be separated by adding saturated sodium chloride solution; it is completely decomposed at the ordinary temperature by sodium carbonate or sodium hydroxide. That the elements of sodium hydrogen sulphite are attached to the aldehyde group is proved by the fact that the additive compound, when treated with phenylhydrazine acetate, yields citronellal phenylhydrazone, and with semicarbazide hydrochloride yields *citronellal semicarbazone*,



in the form of plates melting at  $84^\circ$ . A *dihydrosulphonic acid*,  $\text{SO}_3\text{Na}\cdot\text{C}_9\text{H}_{18}\cdot\text{CH}(\text{OH})\cdot\text{SO}_3\text{Na}$ , is obtained when the aldehyde or the above-mentioned additive product is treated with a sufficient quantity of warm, sodium hydrogen sulphite solution containing sodium sulphite. When warmed with dilute sodium hydroxide, the disulphonic acid yields the sodium salt of a *monhydrosulphonic acid*,  $\text{SO}_3\cdot\text{C}_9\text{H}_{18}\cdot\text{COH}$ , which is not decomposed by boiling with sodium hydroxide solution. Its constitution must be either



or  $\text{CHMe}_2\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COH}$ .

[With GEORG LEMME.]—Specimens of citral, obtained by five different methods, all exhibited the same properties, and gave identical derivatives. The normal additive compound of citral and sodium hydrogen sulphite is obtained when citral (100 parts),  $\text{Na}_2\text{S}_2\text{O}_3 + 7\text{H}_2\text{O}$  (100 parts), water (200 parts), and acetic acid (25 parts) are well shaken; it is decomposed on dissolving it in water, but may be recrystallised from methylic alcohol containing a little acetic acid; a theoretical yield of citral can never be obtained from the compound. Citryl- $\beta$ -naphthacinchonic acid melts at  $199\text{--}200^\circ$ . A *stable dihydrosulphonic acid* derivative of citral is obtained when the normal compound is subjected to steam distillation or is boiled with chloroform, half the citral being regenerated; it readily reacts with phenylhydrazine, but a pure phenylhydrazone has not been obtained, neither has the constitution as yet been settled. A *labile dihydrosulphonic acid* is obtained when citral is shaken with sodium sulphite, and the sodium hydroxide which is set free is neutralised. It is readily soluble in water, and is decomposed by an excess of alkali. It may be shown to contain the aldehyde group, since it reacts with semicarbazide, yielding *sodium citralsemicarbazonedihydrodisulphonate*. A detailed description of the method for the preparation of this labile disulphonic acid is given, and also a method by means of which citral may be titrated with sulphuric acid and sodium sulphite. When the disulphonic acid

is evaporated in the presence of a small quantity of alkali, it loses the elements of sodium sulphite, and unaltered citral is regenerated ; in purifying citral, it suffices to form the labile disulphonic compound in solution, and then decompose with alkali. The labile compound is moderately stable in the presence of acids, but by prolonged action becomes converted into the isomeric stable compound. *Sodium citral-hydrosulphonate*, obtained when the labile dihydrodisulphonate is shaken with citral, is more readily soluble in methylic alcohol than the sodium salt of the disulphonate, and is immediately decomposed by sodium hydroxide. J. J. S.

**Detection and Estimation of Citral.** By FERDINAND TIEMANN (*Ber.*, 1898, 31, 3324—3340).—In the Doebner citral test (*Abstr.*, 1894, i, 262, 532), in addition to citryl- $\beta$ -naphthacinchonic acid (m. p.  $310^{\circ}$ ), two other products are also formed, namely,  $\alpha$ -methyl- $\beta$ -naphthacinchonic acid and the  $\beta$ -naphthalide of *methylnaphthacinchonic acid* melting at  $230$ — $232^{\circ}$ . The amount of citryl naphthacinchonic acid is usually about 46 per cent. of the theoretical; the acid crystallises in a pure state when sufficient citral is present, but otherwise methyl- $\beta$ -naphthacinchonic acid also crystallises with it. It follows that Doebner's reaction is an extremely good test for citral, but the presence of products of higher melting point cannot be taken to indicate the presence of another aldehyde. Oils containing citral yield some 80—85 per cent. of their citral in the form of the cinchonic acid, but with oils containing only small quantities of citral, the above-mentioned products of higher melting point are formed, and the method can no longer be used as a quantitative process. The detection of citronellal in the presence of citral can only be depended on when 10 per cent. at least of the former is present.

*Citralidenecyanacetic acid*,  $C_9H_{15}\cdot CH:C(CN)\cdot COOH$ , obtained when cyanacetic acid is shaken with citral in the presence of aqueous sodium hydroxide, separates, on acidifying, as an oil which rapidly solidifies; in the crude form, it melts at  $85$ — $90^{\circ}$ , but, after recrystallisation from benzene, at  $122^{\circ}$ . About 92—95 per cent. of the theoretical quantity of the crude acid is obtained, and citral in various oils may be estimated by this method.

When treated in the usual manner with semicarbazide, citral gives a mixture of two semicarbazones, of which one, crystallising in needles and melting at  $164^{\circ}$ , is first deposited, the amount being some 60—70 per cent.; the aqueous mother liquor contains a second semicarbazone crystallising in plates and melting at  $171^{\circ}$ . A mixture of the compound of low melting point with some 6—10 per cent. of the other melts at  $135^{\circ}$ , the melting point of the crude citral semicarbazone. The semicarbazones cannot be employed as a basis for a method for estimating citral.

According to the author, the best methods for estimating citral are : (1) conversion into citralidenecyanacetic acid ; (2) conversion into the normal sodium hydrogen sulphite derivative ; (3) conversion into the labile sodium citraldihydrodisulphonate (see preceding abstract). The other constituents of lemon grass and similar oils, for example, geraniol, linalool, and hydrocarbons, do not appear to combine with sodium

hydrogen sulphite. The sulphite method is employed by Schimmel and Co. for estimating cinnamaldehyde in oil of Cassia and citral in lemon grass oil. J. J. S.

**Action of Alkaline and Acid Reagents on Citral.** By FERDINAND TIEMANN (*Ber.*, 1899, 32, 107—115).—Citral,



is converted by acids into cymene, and this reaction probably proceeds in several stages, the elements of water being first assumed and then again lost; even on this assumption, it must be supposed that one of the double linkings migrates from a position in one of the side chains into the benzene ring. The first product of the action of acids probably has the constitution  $\text{OH}\cdot\text{CMe}\left\langle\begin{array}{c}\text{CH}_2\text{---CH}_2 \\ \text{CH}_2\cdot\text{CH}(\text{OH})\end{array}\right\rangle\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$ , and is converted by loss of the elements of water into a compound of the formula  $\text{CMe}\left\langle\begin{array}{c}\text{CH}\cdot\text{CH}_2 \\ \text{CH}:\text{CH}\end{array}\right\rangle\text{C}\cdot\text{CMe}_2$ , which then passes into cymene by the migration of the double linking. Unsuccessful attempts have been made by the author to bring about a migration of one of the double linkings of citral without the formation of a benzene ring. Acids such as sulphurous acid, and sulphuric acid in presence of an oxidising agent, acting on an excess of citral, fail to produce any isomeric compound, cymene, resinous products, and unaltered citral being the result of all these reactions. Caustic soda causes a partial decomposition into methylheptenone and acetaldehyde, and also produces resinous substances, but does not bring about the formation of an isomeride. A. H.

**Action of Semicarbazide on Samples of Citral Purified by Different Methods.** By FERDINAND TIEMANN (*Ber.*, 1899, 32, 115—121. Compare preceding abstracts).—Ordinary citral yields two isomeric semicarbazones, one of which is formed in large amount and melts at  $164^\circ$ , whereas the second is produced in small amount only and melts at  $171^\circ$ . When the sodium hydrogen sulphite compound of citral is decomposed by sodium carbonate and shaken two or three times with ether, a portion of the citral is converted into the hydrosulphonic acid derivatives, whilst the remainder, amounting to about one-half of the total amount present, is dissolved by the ether; this fraction of the citral only yields the semicarbazone melting at  $164^\circ$ , and is therefore termed *citral a*. It boils at  $118\text{--}119^\circ$  under a pressure of 20 mm., has a sp. gr. = 0.8898, and an index of refraction 1.4891. In its chemical properties, it behaves in precisely the same way as ordinary citral; thus it can readily be converted into pseudionone, which on inversion yields the ordinary ionone containing both the  $\alpha$ - and  $\beta$ -modifications. The citral obtained by the decomposition of the hydrosulphonic acid derivatives referred to above yields a small amount of semicarbazone melting at  $171^\circ$ , and when repeatedly treated in a similar manner, it yields a much larger proportion of this semicarbazone, amounting finally to about 70 per cent. of the whole; it has not been found possible, however, to obtain a specimen which yields this semicarbazone exclusively. The fraction containing 70 per cent. of *citral b* does not differ in physical pro-

perties from citral  $\alpha$ , and, like this, can be converted into ordinary pseudoionone. Citral  $\beta$  yields the ordinary citralidenecyanacetic acid melting at  $122^\circ$ , but this is accompanied by a substance melting at  $80^\circ$ , probably an isomeride. These results are in favour of the view that ordinary citral contains two geometrical isomerides; it is, however, not impossible that the formation of the semicarbazone melting at  $171^\circ$  may be due to the presence of some hitherto unsuspected impurity, which accumulates in the fraction known as citral  $\beta$ .

A. H.

**Methods of Synthesis derived from the Study of Cyanals (Cyanhydrins of Aldehydes).** By ALBERT COLSON (*Ann. Chim. Phys.*, 1897, [vii], 12, 231—257).—This paper refers to results already published (compare Abstr., 1895, i, 257; 1896, i, 282, 283, 346).

G. T. M.

**Oxidation of Ketones.** By E. VON COCHENHAUSEN (*J. pr. Chem.*, 1898, [ii], 58, 451—457).—In applying Benedikt and Zsigmondy's process (Benedikt-Ulzer, *Analyse der Fette*, 3rd Edt., 184), as modified by Herbig, for the detection of glycerol in purified wool fats, the author always found small amounts of oxalic acid; this was also the case with a specimen of pure wool fat, which had been prepared using acetone as the solvent. As the fat was free from glycerides, it was thought probable that the oxalic acid resulted from the oxidation of acetone, it being particularly difficult to free the fat from the last traces of this substance.

From a study of the action of potassium permanganate on pure acetone, the author finds that in alkaline solution, without heating, and when an insufficiency of the oxidising agent is employed, oxalic acid is the main product; with excess of permanganate, oxalic acid and carbonic anhydride are produced, whilst with very small amounts acetic acid is formed in addition to these two substances. It follows, therefore, that Popoff's law of the oxidation of ketones does not always hold good, and that Benedikt and Zsigmondy's test for the presence of glycerides in fatty mixtures is only of use in absence of acetone.

Experiments are now being made to see whether homologous ketones behave in a similar manner on oxidation.

A. W. C.

**Aliphatic Nitro-compounds with Multiple Functions.** By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 887, and *Rec. Trav. Chim.*, 17, 399—404; from *Bull. Acad. roy. Belg.*, [iii], 36, 149—154).—In continuation of his studies of the dependence of volatility and other properties on constitution, the author and his pupils have prepared compounds which contain the group  $\cdot\text{C}\cdot\text{NO}_2$  and the group  $\cdot\text{CO}$  or  $\cdot\text{CN}$  in the same molecule. *Nitracetone*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$ , prepared by the action of potassium dichromate and sulphuric acid on nitroisopropyl alcohol, is a limpid, colourless liquid with a pungent odour and burning taste; it is very slightly soluble in water, dissolves in alcohol and ether, boils at  $152^\circ$  under 717 mm. pressure, has a sp. gr. = 1.070 at  $14^\circ$ , and liberates carbonic anhydride from carbonates. *Nitrobutyronitrile*,  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2$ , obtained by the action of silver nitrite on iodobutyronitrile, is a

colourless liquid with a faint odour and rather sweet, pungent taste ; it is insoluble in water, easily soluble in alcohol, ether, chloroform, and alkalis, has a sp. gr. = 1.138 at 12°, boils at 160° under 35 mm. pressure, and boils and decomposes at 236° under 760 mm. pressure. By the action of concentrated hydrochloric acid on nitrobutyronitrile at 50°, nitrobutyric acid is formed, whilst at higher temperatures it yields succinic acid and hydroxylamine hydrochloride. The author points out the influence of the various groups on the properties, and especially on the boiling points of the various compounds.

E. W. W.

**Action of Nitrous Acid on Aliphatic Ketones.** By GIACOMO PONZIO and AUSONIO DE-GASPARI (*J. pr. Chem.*, 1898, [ii], 58, 392—402 ; also *Gazzetta*, 1898, 28, ii, 269—279. Compare following abstract).—By the action of nitrous acid on ketones of the structure  $\text{CH}_2\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{R}$  (up to 9 carbon atoms), two isonitroso-ketones are formed, if the ketones have a normal structure, whereas if they have a tertiary structure only one isonitroso-ketone is produced. In the latter case, it is always the hydrogen of the methylene group of the normal alcohol radicle which is displaced by the group NOH.

The structure of the isonitroso-ketones formed was proved by converting them into acyldinitro-hydrocarbons (according to a method already described), and subsequently hydrolysing them, when from a mixture of two isomeric isonitroso-ketones two fatty acids and two dinitro-hydrocarbons are obtained, whereas one isonitroso-ketone gives one fatty acid and one dinitrohydrocarbon.

Ethyl propyl ketone yields two isomeric isonitroso-ketones when treated with amylic nitrite and hydrochloric acid, from which dinitroethane and dinitropropane were obtained and separated by means of their potassium derivatives ; also, by conversion of the mixture into dioximes by Auwer's method, two substances were obtained and characterised by means of their osazones as acetylbutyrylosazone and dipropionyllosazone.

*Ethyl butyl ketone*, prepared by the action of zinc ethyl on valeric chloride, is a pleasant smelling liquid boiling at 147—148° under a pressure of 742.9 mm. When treated with amylic nitrite, it yields two isonitroso-ketones, which were characterised by conversion into dinitroethane and dinitrobutane respectively.

Ethyl amyl ketone, prepared from zinc ethyl and normal hexoic chloride, gives two isomeric isonitroso-ketones, yielding dinitroethane and dinitropentane respectively.

*Ethyl iso-amyl ketone*, obtained by the action of zinc ethyl on isobutyric chloride (b. p. 143—145° under 741.53 mm.), is a pleasant smelling liquid boiling at 163—163.5° under a pressure of 734.2 mm. Amylic nitrite converts it only into *isonitrosoethyl isoamyl ketone*,  $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CMe}\cdot\text{NOH}$ , a pale, yellow oil. By the action of hydroxylamine, it is converted into acetylisohexyldioxime melting at 177—178°.

*Ba-Acetylisohexyphenylhydrazoxime*,  $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CMe}\cdot\text{NOH}$ , prepared from the isonitroso-ketone and phenylhydrazine, crystallises from dilute alcohol in colourless leaflets melting at 113—114°.

*Ba-Acetylisohexyphenylhydrazone*, obtained from the phenylhydraz-

oxime by boiling with alcohol and hydrochloric acid, crystallises from alcohol in small, almost colourless needles melting at 92—93°. When heated at 150° with phenylhydrazine, it is converted into acetyliso-hexylosazone melting at 92—93°.

*Ethyl isoheptyl ketone*, obtained by the action of zinc ethyl on isoheptioic chloride (isoamylacetic chloride, b. p. 168—169° under 739·44 mm.), is a fruity smelling liquid boiling at 185° under a pressure of 740·32 mm. Amylic nitrite converts it into *isonitrosoethyl isoheptyl ketone*, a pale yellow oil.

*Acetylisoheptyldioxime* (acetylisoamylacetyldioxime),



crystallises from alcohol in white needles melting at 169—170°.

$\beta$ -*Acetylisoheptylphenylhydrazoxime* crystallises from alcohol in pale yellow leaflets melting at 115—116°, and *acetylisoheptylosazone* forms yellow prisms melting at 133—134°.

A. W. C.

**Acetylcaproyl [Methyl Amyl Diketone].** By GIACOMO PONZIO and O. PRANDI (*J. pr. Chem.*, 1898, [ii], 58, 401—402; also *Gazzetta*, 1898, 28, ii, 279—283. Compare preceding abstract).—*Acetylhexoyl* (2:3-octadione),  $\text{C}_5\text{H}_{11}\cdot\text{CO}\cdot\text{CMe}$ , prepared from its monoxime, isonitrosomethyl hexyl ketone, by the action of dilute sulphuric acid, is a yellow liquid boiling at 172—173° under a pressure of 732·8 mm.

$\alpha\beta$ -*Acetylhexoylphenylhydrazoxime*,  $\text{C}_5\text{H}_{11}\cdot\text{C}(\text{NOH})\cdot\text{CMe}:\text{N}_2\text{HPh}$ , crystallises from dilute alcohol in yellow needles melting at 110°.

$\alpha$ -*Acetylhexoylphenylhydrazone* forms glistening, yellow leaflets melting at 103—104° and *acetylhexoylosazone* yellowish-brown prisms melting at 117—118°.

A. W. C.

**Isomorphous Formates of Calcium, Strontium, Barium, and Lead.** By A. PLATHAN (*Chem. Centr.*, 1898, ii, 1009; from *Diss. Helsingfors*, 1897, 46).—The formates of calcium, strontium, barium, and lead were prepared in crystals by evaporating their solutions at 10° and 73°, and by slowly cooling solutions saturated at 100°. These salts are isomorphous and crystallise in rhombic, sphenoidal forms, and not in holohedral forms, as hitherto supposed; the densities and equivalent volumes were determined and the topic axes (Muthmann) and crystal volumes (Schrauf) were calculated. The equivalent volumes of the formates, like those of the sulphates and carbonates, increase from the calcium through the strontium and lead salts to the barium, that of the lead salt being nearly equal to that of the strontium salt. The topic  $\psi$ -axis shows a similar variation, but lead formate has the largest refractive index and molecular refraction. The solubility of the salts at 25° was determined; a complete series of crystalline mixtures of the lead and barium salts were prepared at 25°, and from analyses of the salts and the mother liquors, a curve was plotted, showing the relationship of the composition of the crystals and the solution. Strontium formate crystallises with  $2\text{H}_2\text{O}$  at the ordinary temperature, but if the solution is evaporated at above 71·9°, the anhydrous salt separates. By allowing mixed solutions of the strontium and lead salts to crystallise at 25°, it was found that when 79 per cent. or less of the former salt was present, a mixture of

anhydrous salts crystallises, whilst from solutions containing a larger proportion of this salt a mixture of formates containing  $2\text{H}_2\text{O}$  was obtained.

E. W. W.

**Fluorodibromacetic Acid.** By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1898, ii, 702—704; from *Bull. Acad. roy. Belg.*, [iii], 35, 849—868. Compare Abstr., 1898, i, 457).—Fluorodibromacetic fluoride may be prepared by heating a mixture of tribromacetic chloride (3 mols.: obtained by the action of phosphorus pentachloride on tribromacetic acid), antimony fluoride (2 mols.), and bromine ( $\frac{1}{3}$  mol.) in a platinum vessel. The action takes place slowly, for in one case after 14 days only  $\frac{1}{8}$ ths of the antimony fluoride was found to have been attacked. After removing the excess of bromine by cautiously adding powdered antimony and distilling off the antimony bromide, the product, when fractionated, yields fluorochlorobromacetic fluoride, which distils at  $51^\circ$  and fluorodibromacetic fluoride; the former is probably formed by the action of the antimony chloride, which may result from the action of the fluoride on tribromacetic chloride, on a portion of the fluorodibromacetic fluoride. The latter is a colourless liquid with a pungent odour, boils at  $74.5^\circ$ , acts violently on alcohol and water, but only attacks glass at a high temperature. Its vapour density was determined. From 200 grams of tribromacetic chloride only about 30 grams of fluorodibromacetic fluoride is obtained, tribromacetic chloride, tribromacetic fluoride, derivatives of fluorochlorobromacetic acid, and probably of dibromacetic acid being also formed. Fluorodibromacetic acid is also obtained as a bye-product in the preparation of fluorochlorobromacetic acid. Fluorodibromacetic acid is prepared by adding ice to fluorodibromacetic fluoride cooled to  $-25^\circ$ , removing the water and hydrogen fluoride by keeping the product in a vacuum over alkali, and finally distilling under a pressure of 50—60 mm. It is a strong acid, forms colourless crystals, is very hygroscopic, melts at  $26.5^\circ$ , boils at  $130^\circ$  under 60 mm. and at  $198^\circ$  under 760 mm. pressure, is easily soluble in water and alcohol, and soluble in ether and chloroform. When an aqueous solution of the acid or its salts is boiled, fluorodibromomethane is formed. All the salts are easily soluble in water and alcohol, and when heated leave a residue of bromide; the sodium salt crystallises best from a mixture of alcohol and ether; the potassium salt crystallises from alcohol in leaflets and is not hygroscopic, and the barium salt contains  $6\text{H}_2\text{O}$ . Ethylic fluorodibromacetate is a colourless liquid with a pleasant odour like that of camphor, boils at  $173^\circ$ , has a sp. gr. = 1.7851 at  $12^\circ$  and = 1.77097 at  $30^\circ$ ; its vapour density was determined. *Fluorodibromacetamide*, prepared by shaking ethylic fluorodibromacetate with a saturated solution of ammonia, crystallises from water in prisms, melts at  $136^\circ$ , sublimes at  $100^\circ$ , and is slightly soluble in water, being more soluble than fluorodichloracetamide. The conductivity and amount of dissociation of solutions of fluorodibromacetic acid and tribromacetic acid and the conductivity of solutions of their sodium salts were determined. Of the substituted acetic acids, those containing fluorine are the strongest acids, and fluorodibromacetic acid is a stronger acid than either fluorochlorobromacetic or fluorodichloracetic acid. The substitution



of bromine for chlorine has apparently no influence on the strength of the acid. E. W. W.

**Alkylie Salts of the Monochloro-derivatives of Normal Butyric Acid and the Volatility of Chlorine and Oxygen Compounds.** By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 273; from *Bull. Acad. roy. Belg.*, [iii], 35, 507—520).—The author has prepared the methylic, allylic, and propylic salts of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -chlorobutyric acids by the action of the corresponding alcohols on the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -chlorobutyronitriles (see this vol., i, 183) respectively; the vapour densities of the compounds and their physical constants were determined. The boiling points of these derivatives show that the greater the proximity of the chlorine and oxygen atoms in the molecule, the lower the boiling point; in the  $\gamma$ -derivatives this influence is no longer apparent. The  $\beta$ -chloro-derivatives can also be prepared by the action of hydrochloric acid on the corresponding alkylie salts of crotonic acid or by the direct chlorination of the butyrates. E. W. W.

**Solidifying Points of Mixtures of Stearic and Palmitic Acids.** By L. E. O. DE VISSER (*Rec. Trav. Chim.*, 1898, 17, 346—348. Compare *Abstr.*, 1898, i, 560).—When 100 grams of a mixture of palmitic and stearic acids, containing 47.5 per cent. of the latter, is agitated in the form of thin shreds with 600 c.c. of absolute alcohol during 2 minutes, the solidifying point ( $56.4^\circ$ ) of the portion remaining undissolved does not differ from that of the original mixture; the latter, therefore, must be considered as a solid solution existing in only one form of crystalline aggregation. The eutectic mixture of the two acids, which solidifies at  $54.82^\circ$  and contains 29.76 per cent. of stearic acid (*loc. cit.*), is shown, however, to be a mixture of two solid modifications by its melting at  $55.09^\circ$  after being agitated with absolute alcohol; this melting point corresponds with that of a mixture containing 31.78 per cent. of stearic acid, so that the modification more easily soluble in alcohol must contain a greater amount of stearic acid than that originally present in the eutectic mixture. W. A. D.

**Constitution of the Crotonic Acids.** By FRITZ FICHTER and A. KRAFFT (*Chem. Centr.*, 1898, ii, 1011, from *Arch. Sci. phys. nat. Genève*, [iv], 6, 402—403).—Since  $\beta$ -hydroxyglutaric acid, when distilled in a vacuum, yields, not only glutaric acid, but also isocrotonic acid, the latter must have a constitution corresponding with vinylacetic acid,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{COOH}$ , and hence the crotonic acids are not stereoisomerides, but differ constitutionally in the position of the double bond. E. W. W.

**Derivatives of Aliphatic Hydroxynitriles.** By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 661—662; from *Bull. Acad. roy. Belg.*, [iii], 36, 22—30. Compare this vol., i, 182).

I. HYDROXYNITRILES CONTAINING  $\text{C}_4$ .

$\alpha$ -Methylactonitrile,  $\text{CN}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , is prepared by the action of potassium cyanide on the monochlorhydrin,  $\text{CHMeCl}\cdot\text{CH}_2\cdot\text{OH}$ , or by the addition of hypochlorous acid to propylene; it boils at  $230$ — $235^\circ$ .

*Dimethylglycollonitrile* or *dimethylacetonecyanhydrin*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CN}$ , is obtained by the combination of hydrogen cyanide with dimethyl ketone; by the action of acetic chloride, it yields the *acetate*,  $\text{OAc} \cdot \text{CMe}_2 \cdot \text{CN}$ , a colourless liquid, which boils at  $180\text{--}182^\circ$ , has a sp. gr. =  $0.997$  at  $19^\circ$ , and with phosphoric anhydride yields the *nitrile* of  $\alpha$ -methylacrylic acid (see following abstract). By the action of phosphorus pentachloride on dimethylglycollonitrile, *chloracetoneitrile*,  $\text{CMe}_2\text{Cl} \cdot \text{CN}$ , and the nitrile of  $\alpha$ -methylacrylic acid are obtained.

## II. HYDROXYNITRILES CONTAINING $\text{C}_5$ .

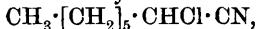
*Isobutylidenecyanhydrin*,  $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CN}$ , prepared by the action of hydrogen cyanide on isobutaldehyde, with phosphorus pentachloride, yields  $\alpha$ -chlorisopropylacetoneitrile,  $\text{CHMe}_2 \cdot \text{CHCl} \cdot \text{CN}$ , which is a limpid, colourless liquid, has an odour like that of amylic compounds, boils at  $154^\circ$  under 750 mm. pressure, has a sp. gr. =  $0.9922$  at  $10^\circ$ , and when distilled with phosphoric anhydride, yields the *nitrile* of  $\beta$ -dimethylacrylic acid (see following abstract). A comparison of the isobutyl with the normal butyl derivatives shows that the introduction of a chlorine atom into the group  $\text{CH}_2 \cdot \text{CN}$ , raises the boiling point about  $24^\circ$ , whilst the introduction of another methyl group into the group  $\text{CH}_2\text{Me}$  raises the boiling point about  $12^\circ$ . *Cyanobutyryl acetate*,  $\text{CHMe}_2 \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$ , is a colourless liquid with an unpleasant, bitter taste, boils at  $192\text{--}193^\circ$ , and has a sp. gr. =  $0.9745$  at  $19^\circ$ .

## III. HYDROXYNITRILES CONTAINING $\text{C}_6$ .

By the action of phosphorus pentachloride, isovalerylcyanhydrin *monochlorisobutylacetoneitrile* or  $\alpha$ -chlorocapronitrile, is converted into  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHCl} \cdot \text{CN}$ ; this is a colourless liquid of pleasant odour and pungent taste, boils at  $172\text{--}173^\circ$  under 755 mm. pressure, has a sp. gr. =  $0.984$  at  $12^\circ$ , is insoluble in water, and by the action of acetic chloride yields *cyanisovaleryl acetate*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$ , a colourless, limpid liquid which boils at  $204^\circ$  and has a sp. gr. =  $0.960$  at  $19^\circ$ . By the action of phosphoric anhydride on amyldene cyanhydrin, the unsaturated nitrile,  $\text{CHMe}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CN}$  (see following abstract) is obtained.

## IV. HYDROXYNITRILES CONTAINING $\text{C}_8$ .

By the action of phosphorus pentachloride on *ænanthylidenecyanhydrin*,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OH}) \cdot \text{CN}$ , prepared by the addition of hydrogen cyanide to *ænanthaldehyde*.  $\alpha$ -chlorocapronitrile,



is obtained as a colourless liquid with an odour like *ænanthaldehyde*; it boils at  $124^\circ$  under 38 mm., and at  $217^\circ$  under 755 mm. pressure, and has a sp. gr. =  $0.959$  at  $12^\circ$ .  $\alpha$ -Acetylænanthylidenecyanhydrin,  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$ , is a colourless liquid, with a bitter taste, boils at  $245^\circ$ , and has a sp. gr. =  $0.9385$  at  $19^\circ$ . E. W. W.

**Unsaturated Compounds.** By LOUIS HENRY (*Chem. Centr.*, 1898, ii, 662—663; from *Bull. Acad. roy. Belg.*, [iii], 36, 31—54).

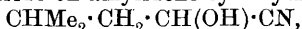
## I. UNSATURATED NITRILES.

By the action of phosphoric anhydride on hydroxynitriles, unsaturated nitriles are often formed, but lactoneitrile,  $\text{CN} \cdot \text{CHMe} \cdot \text{OH}$ , does not yield acrylonitrile.

*Unsaturated Nitriles containing C<sub>4</sub>.*—The hydroxynitriles containing C<sub>4</sub>, with one exception, when heated with phosphoric anhydride, lose 1H<sub>2</sub>O. Acetonecyanhydrin or dimethylglycollonitrile gives a good yield of *α*-methylacrylonitrile, CH<sub>2</sub>:CMe·CN, which is a colourless, limpid liquid with a strong odour and a bitter taste, boils at 90—92°, has a sp. gr. = 0·7991 at 18°, and is insoluble in water. By comparing the corresponding nitriles, it is seen that the saturated nitriles containing C<sub>3</sub> boil about 20°, and the saturated nitriles containing C<sub>4</sub> about 18° higher than the unsaturated nitriles. By the action of phosphoric anhydride on *α*- or *β*-hydroxybutyronitrile, *β*-methylacrylonitrile, CHMe:CH·CN, is formed; this boils at 118—119°; *γ*-hydroxybutyronitrile is completely charred by the action of phosphoric anhydride. Vinylacetoneitrile, CN·CH<sub>2</sub>:CH:CH<sub>2</sub>, prepared by distilling the chloride, CN·CH<sub>2</sub>:CH<sub>2</sub>:CH<sub>2</sub>Cl, with dry potassium hydroxide, is a colourless liquid with a pleasant odour and pungent taste; it boils at 135° and has a sp. gr. = 0·911 at 16°.

*Unsaturated Nitriles containing C<sub>5</sub>.*—By the action of phosphoric anhydride on isobutyridene cyanhydrin, *β*-dimethylacrylonitrile, CN·CH:CMe<sub>2</sub>, is obtained; it is a colourless liquid with a pleasant odour and a pungent taste, boils at 140—142°, has a sp. gr. = 0·8292 at 14°, is insoluble in water and soluble in alcohol and ether.

*Unsaturated Nitriles containing C<sub>6</sub>.*—*γ*-Dimethylcrotononitrile or *β*-isopropylacrylonitrile, CHMe<sub>2</sub>:CH:CH·CN, prepared by the action of phosphoric anhydride on amyridene cyanhydrin,



is a colourless liquid with a pleasant odour, boils at 154—155° under 754 mm. pressure, has a sp. gr. = 0·8268 at 16°, is insoluble in water, and soluble in alcohol, ether, &c.

*Unsaturated Nitriles containing C<sub>8</sub>.*—By the action of phosphoric anhydride on *α*-naphthylidene cyanhydrin, *γ*-butylcrotononitrile, CH<sub>3</sub>: [CH<sub>2</sub>]<sub>4</sub>:CH:CH·CN, is formed; it is a colourless liquid with an unpleasant taste, boils at 197—200°, has a sp. gr. = 0·8318 at 16°, is insoluble in water, but soluble in alcohol and ether. The unsaturated nitriles containing C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> have the same boiling points as the corresponding saturated nitriles.

In the original paper, tables showing the influence of the substitution of a methyl group for a hydrogen atom, on the boiling points of unsaturated nitriles, and tables showing the boiling points of the corresponding saturated and unsaturated nitriles, are given for each series.

## II. DERIVATIVES OF CROTONIC ACID.

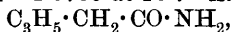
*Crotonic chloride*, CHMe:CH·COCl, prepared by the action of phosphorus pentachloride on crotonic acid, is a colourless, fuming liquid with an oppressive odour, boils at 124—125°, and has a sp. gr. = 1·295 at 16°.

*Ethyl β-chlorobutyrate*, CHMeCl·CH<sub>2</sub>:COOEt, is obtained by the action of alcohol on crotonic chloride, or by adding hydrochloric acid to ethylic crotonate; it boils at 165—170°.

## III. A. DERIVATIVES OF ALLYLACETIC ACID. [With CAMILLE ASCHMANN, *Diss. Löwen*, 1883].

Allylacetic acid is prepared by boiling ethylic allylacetate with the calculated quantity of a solution of 140 parts of potassium hydroxide

in 40 parts of water; the *chloride*,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COCl}$ , obtained by the action of phosphorus trichloride on the acid, is a thin, colourless, fuming liquid with an oppressive odour, boils at  $128^\circ$  under 765 mm. pressure and has a sp. gr. = 1.0739 at  $16^\circ$ . *Allylacetylamide*,



crystallises in white leaflets, melts at  $94^\circ$ , boils at  $230^\circ$  under 770 mm. pressure and is soluble in water, alcohol, and ether. *Allylacetonitrile*,  $\text{C}_3\text{H}_5\cdot\text{CH}_2\cdot\text{CN}$ , has a pleasant odour, boils at  $140^\circ$ , has a sp. gr. = 1.1803 at  $13^\circ$ , and is insoluble in water. The allylacetyl derivatives have the same boiling points as the corresponding valeryl derivatives. *Chlorhydroxyvaleric acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , prepared by the union of hypochlorous acid with allylacetic acid, is a colourless liquid, heavier than water, decomposes on heating, and is slightly soluble in water. Ethylic allylacetate combines with iodine monochloride in aqueous solution, forming crystals which melt at  $61^\circ$ .

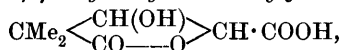
*B. Allylacetone*,  $\text{C}_3\text{H}_5\cdot\text{CH}_2\cdot\text{COMe}$ .—This can be prepared by boiling ethylic allylacetate with aqueous potassium carbonate solution; it combines easily with hypochlorous acid to form the *chlorhydrin*,  $\text{OH}\cdot\text{C}_3\text{H}_5\text{Cl}\cdot\text{CH}_2\cdot\text{COMe}$ , a colourless, viscous liquid, which cannot be distilled under the ordinary pressure, and is heavier than water.

*C. Fumaric acid*.—By the action of hypochlorous acid on ethylic fumarate, *ethylic dichlorosuccinate*,  $\text{C}_2\text{H}_2\text{Cl}_2(\text{COOEt})_2$ , is formed; it crystallises in colourless needles and melts at  $57^\circ$ . Since hypochlorous acid does not combine with ethylic fumarate, whilst it easily unites with ethylene, the displacement of a hydrogen atom by the  $\text{COOEt}$  group apparently lessens the additive power of an unsaturated compound. Perchlorethylene does not combine with hypochlorous acid.

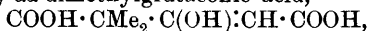
E. W. W.

**Methylic  $\gamma$ -Cyanodimethylacetoacetate.** By MAX CONRAD and RICHARD GAST (*Ber.*, 1899, 32, 137—145. Compare Lawrence, *Proc.*, 1898, 251).—The cyanogen radicle in this compound can be displaced in the same manner as the bromine in methylic  $\gamma$ -bromodimethylacetoacetate; thus, with aqueous thiourea, it forms hydrocyanic acid and methylic amidothiazylisobutyrate, whilst with piperidine it gives methylic  $\gamma$ -piperidylidimethylacetoacetate; with aniline, it gives methylic  $\gamma$ -anilidodimethylacetoacetate, which loses methylic alcohol and is converted into phenyldimethylketopyrrolidone,  $\text{NPh}\begin{matrix} \text{CH}_2\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{CO}-\text{CMe}_2 \end{matrix}$ .

On hydrolysis with hydrochloric acid or with baryta, an acid,  $\text{C}_7\text{H}_{10}\text{O}_5$ , is obtained. This melts at  $214^\circ$ , and the authors show that it is the monolactone of  $\beta\gamma$ -dihydroxy- $\alpha\alpha$ -dimethylglutaric acid,



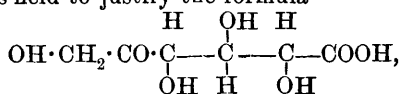
and not  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylglutaconic acid,



as was supposed by Lawrence. The *barium* salt, *calcium* salt,  $\text{Ca}(\text{C}_7\text{H}_9\text{O}_5)_2\cdot 4\text{H}_2\text{O}$ , and *silver* salt,  $\text{AgC}_7\text{H}_9\text{O}_5$ , were prepared. The lactone can be hydrolysed by boiling with baryta water, when the *barium* salt of  $\beta\gamma$ -dihydroxy- $\alpha\alpha$ -dimethylglutaric acid is produced; the

corresponding acid could not be isolated. The acid,  $C_7H_{10}O_4$ , prepared by the action of hydriodic acid on the acid  $C_7H_{10}O_5$ , is regarded by the authors as the lactone of *αα*-dimethyl- $\gamma$ -hydroxyglutaric acid,  $CMe_2 \cdot CH_2 \cdot CO \text{---} O > CH \cdot COOH$ , whilst Lawrence regarded it as *αα*-dimethylglutaconic acid,  $COOH \cdot CH \cdot CH \cdot CMe_2 \cdot COOH$ . T. M. L.

**Products of Oxidation of Hydroxygluconic Acid.** By LÉON BOUTROUX (*Compt. rend.*, 1898, 127, 1224—1227).—The author has isolated a hydroxygluconic acid as a product of oxidation of gluconic acid by a bacterium in presence of calcium carbonate. The acid, which closely resembles a hydroxygluconic acid recently obtained by Bertrand (*Proès-verbal Soc. Chim.*, Nov. 11, 1898), may be oxidised with dilute nitric acid, affording racemic acid, a trihydroxyglutaric acid, glyoxylic acid, and  $\alpha\beta$ -dihydroxybutyric acid. The formation of these substances is held to justify the formula



as representing the structure of the hydroxygluconic acid in question. A. L.

**Action of Ethylic Malonate on Unsaturated Ketones.** By DANIEL VORLÄNDER and S. GÄRTNER (*Annalen*, 1898, 304, 1—24. Compare Abstr., 1897, i, 272).—Phorone behaves differently towards ethylic sodiomalonate according as the latter is dissolved in absolute alcohol or is suspended in ether.

*Phoronediacetic acid*,  $CO(CH_2 \cdot CMe_2 \cdot CH_2 \cdot COOH)_2$ , is prepared by adding phorone to ethylic sodiomalonate (2 mols.), suspended in ether or benzene, and heating the mixture during 24 hours at the boiling point of ether; it crystallises from boiling water in lustrous leaflets, or long, flattened needles, and melts at  $110^\circ$ . The *barium* salt forms prisms containing  $3H_2O$ , and the *silver* salt resists the action of light; the *methylic* salt boils at  $183\text{--}184^\circ$  under a pressure of 25 mm. The *oxime* crystallises from water in aggregates of prisms, and melts at  $141\text{--}143^\circ$ ; the *anhydride* melts at  $49^\circ$ . The acid is but slowly attacked by a cold solution of potassium permanganate, but at  $70\text{--}100^\circ$ , in presence of sodium carbonate, it becomes oxidised to unsymmetrical dimethylsuccinic acid; the latter is also produced when dimethylhydroresorcinol is oxidised with potassium permanganate.

The *anhydride*,  $C_9H_{12}O_4$ , is a bye-product in the preparation of phoronediacetic acid, and is also produced during the formation of dimethylhydroresorcinol from mesitylic oxide and ethylic malonate; it crystallises in prisms, or needles, and melts at  $135^\circ$ .

$\gamma$ -*Acetyl- $\beta\beta$ -dimethylbutyric acid*,  $COMe \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot COOH$ , is another product of the action of phorone on ethylic sodiomalonate; the *methylic* salt boils at  $215^\circ$ , and the *semicarbazone* crystallises from boiling water in prisms, and melts at  $172^\circ$ , when it decomposes.

The *anhydride*,  $C_{13}H_{18}O_4$ , results from the action of ethylic sodio-

malonate on pulegone in molecular proportion ; it crystallises from dilute alcohol in prisms, and melts at  $104^{\circ}$ .

Methylcyclohexenone is indifferent towards ethylic sodiomalonate.

M. O. F.

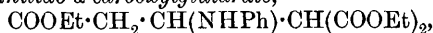
**Triethylic Isaconitate** ( $\omega_2$ - $\Delta$ - $\omega_1$ -Propenetricarboxylate). By MAX GUTHZEIT and LEOPOLD LASKA (*J. pr. Chem.*, 1898, [ii], 58, 403—441).—Ethylic isaconitate (ethylic  $\omega_2$ - $\Delta$ - $\omega_1$ -propenetricarboxylate),  $C_{12}H_{18}O_6$ , prepared from ethylic ethoxycoumalindicarboxylate by the method already given (*Abstr.*, 1889, 860), boils at  $176$ — $178^{\circ}$  under a pressure of 17 mm. The dry *sodium* derivative is a reddish-yellow powder, soluble in water, forming a yellow solution, which gives precipitates with copper, silver, cadmium, lead, cobalt, nickel, zinc, and barium salts.

*Ethylic ethylisaconitate*,  $CEt(COOEt)_2 \cdot CH:CH \cdot COOEt$ , obtained by the action of sodium and ethylic iodide on ethylic isaconitate in alcoholic solution, is an oil boiling at  $176$ — $177^{\circ}$  under a pressure of 18 mm. The corresponding *benzyl* derivative is a colourless oil boiling at  $237$ — $239^{\circ}$  under a pressure of 23 mm.

When ethylic isaconitate is hydrolysed with hydrochloric acid, 50 per cent. of the theoretical amount of glutaconic acid is obtained, together with hydroxyglutaric acid and butyrolactonecarboxylic acid ; potassium hydroxide in the cold produces the same effect, the absence of malonic acid in both cases showing that the chain has not been broken. With barium hydroxide, the chain is broken, for besides glutaconic and hydroxyglutaric acids, malonic, acetic, and formic acids are also produced.

When heated with aniline at  $150^{\circ}$ , ethylic isaconitate is decomposed into malonamide, and a substance which could not be obtained pure, but which is possibly the anilide of  $\beta$ -anilidoacrylic acid ; paraluidine reacts in an analogous manner.

*Triethylic  $\beta$ -anilido- $\alpha$ -carboxylglutarate*,



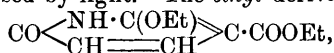
is obtained as a yellow oil by the action of aniline on ethylic isaconitate in the cold ; ferric chloride gives a black coloration with it. The *hydrochloride*,  $C_{16}H_{25}NO_6 \cdot HCl$ , separates from absolute ether in needle-shaped crystals which melt at  $160^{\circ}$ , resolidify at once, and melt for the second time at  $176$ — $177^{\circ}$  ; this is probably due to the elimination of alcohol with formation of an oxyquinoline derivative. It is decomposed by water, and yields ethylic malonate when heated to  $150^{\circ}$ .

Ethylamine acts on ethylic isaconitate in a similar manner to aniline, even when very dilute, with formation of malonodiethylamide ; ammonia never produces a fission of the carbon chain, but leads to the formation of ring compounds, which can be readily explained on the assumption that the ethereal salt exists in the enolic form.

The *ammonium* derivative of *ethylic 2-hydroxy- $\Delta_{2,4}$ -hydropyridone-3-carboxylate*,  $\begin{array}{c} CO \cdot NH \cdot C \cdot O \cdot NH_4 \\ | \\ CH:CH \cdot C \cdot COOH \end{array}$ , obtained by the action of a satu-

rated aqueous solution of ammonia on ethylic isaconitate at  $0^{\circ}$ , is a light yellow powder which becomes red when heated to  $200^{\circ}$ , and

melts about  $215^{\circ}$ . When boiled with alkalis, ammonia is eliminated, and when dissolved in concentrated hydrochloric acid, and then treated with water, it gives rise to *ethylic 2-hydroxy- $\Delta_{2,4}$ -hydropyridone-3-carboxylate*,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{OH}) \\ \text{CH} = \text{CH} \end{smallmatrix} \text{C} \cdot \text{COOEt}$ , which crystallises from acetone in glistening, silken needles, melts at  $183^{\circ}$ , gives a blood-red coloration with ferric chloride in alcoholic solution, but does not give a precipitate with picric acid. The ammonium salt gives precipitates with silver, copper, lead, zinc, barium, and magnesium salts. When fused with phthalic anhydride, the melt dissolves in water with a red coloration, and gives a beautiful blue fluorescence with ammonia, a reaction which Ruhemann (Trans., 1893, 259) has shown to be characteristic for metadihydroxypyridine. The basic properties of this substance are very slight. The *silver* salt prepared from the sodium derivative by the action of silver nitrate is a white substance not readily decomposed by light. The *ethylic* derivative,



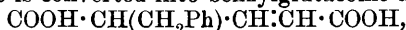
obtained from the silver salt by interaction with ethylic iodide, separates from light petroleum in white crystals melting at  $66-67^{\circ}$ . Ferric chloride colours the alcoholic solution yellowish-red.

*2-Hydroxy- $\Delta_{2,4}$ -hydropyridine-3-carboxylic acid*, prepared from the ethylic salt by the action of concentrated sulphuric acid, crystallises in needles, melts in a closed tube at  $197-198^{\circ}$ , gives no blue coloration with potassium nitrite, and its ammoniacal solution gives precipitates with silver, copper, lead, and barium salts. It is isomeric, not identical with Ost's comenamic acid (Abstr., 1883, 792). Bromine oxidises the acid, but with the ethylic salt, gives a *substitution product*,  $\text{C}_8\text{H}_8\text{O}_4\text{NBr}$ , which is coloured bluish-black, without melting, when heated to  $210^{\circ}$ .

When the ethylic salt is heated at  $250-260^{\circ}$  with phosphorus pentachloride and phosphorus oxychloride in sealed tubes, it is converted into *aa'-dichloronicotinic acid*,  $\text{CCl} \begin{smallmatrix} \text{N} - \text{CCl} \\ \text{CH} : \text{CH} \end{smallmatrix} \text{C} \cdot \text{COOH}$ , which separates from ether in yellow crystals melting at  $135-136^{\circ}$ , but from a mixture of ether and light petroleum in white needles melting at  $144^{\circ}$ .

When the mother liquors from the hydrodioxy-pyridine derivative are evaporated, they yield a small amount of the *amide* of hydrodioxy-pyridinecarboxylic acid,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{OH}) \\ \text{CH} = \text{CH} \end{smallmatrix} \text{C} \cdot \text{COOH}$ , melting with evolution of gas at  $206^{\circ}$ .

When hydrolysed with alcoholic potash or barium hydroxide, ethylic benzylisacnitrate is converted into benzylglutaconic acid,



melting at  $150-152^{\circ}$ ; neither aniline nor ammonia produces either an additive product or causes fission of the carbon chains, but substances, probably pyridine derivatives, which readily suffer oxidation are formed.

Ethylic carboxylglutarate (ethylic  $\omega_2\omega_1$ -propanetricarboxylate),  $\text{COOEt} \cdot \text{CH}(\text{COOEt}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOEt}$ , obtained from ethylic isacnitrate by the action of zinc dust and acetic acid, is a liquid boiling

at  $171^{\circ}$  under a pressure of 18 mm. Ferric chloride does not produce a blue colour, and when heated with alcoholic ammonia, *carboxyglutaramide*,  $\text{CONH}_2 \cdot \text{CH}(\text{CONH}_2) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CONH}_2$ , is produced crystallising in needles melting at  $181^{\circ}$ . A. W. C.

**A Double Citrate of Zirconium and Ammonium.** By S. H. HARRIS (*Amer. Chem. J.*, 1898, 20, 871—872).—On adding a 10 per cent. solution of ammonium citrate to an aqueous solution of the mixed chlorides obtained by dissolving zirconium hydroxide in concentrated hydrochloric acid, and repeatedly recrystallising the product, a white, curdy precipitate separates, which very easily dissolves in an excess of ammonium citrate; when dried at  $120^{\circ}$ , it has the composition  $\text{Zr}_2\text{C}_6\text{H}_5\text{O}_7(\text{NH}_4)_3$ , and is very deliquescent. W. A. D.

**Influence of Formation of Salts on the Hydrolysis of Amides and Ethereal Salts by Alkalis.** By EMIL FISCHER (*Ber.*, 1898, 31, 3266—3277).—Among the members of the uric acid group, compounds which contain hydrogen replaceable by metals are much less readily hydrolysed by alkalis than compounds in which the hydrogen has been replaced by methyl or some other group; thus, whilst uric acid itself can be boiled with an excess of normal alkali for a long time without undergoing much decomposition, tetramethyluric acid is rapidly decomposed even in the cold, the mono-, di-, and tri-methyluric acids standing in an intermediate position between these extremes. The ease with which the decomposition can be effected seems also to depend on the constitution of the compound, 1:3:9-trimethyluric acid, for example, being much more readily decomposed than the 1:7:9-derivative. Similar relations hold in the series of the xanthine and hypoxanthine derivatives, as well as among the chloropurines and bromoxanthines. Thus xanthine is much more stable towards alkalis than theobromine, whilst the latter is again more stable than caffeine, and the same gradation exists between the bromine derivatives of these compounds; the same difference has been found to exist in many other series of compounds. Thus cyanuric acid is much more stable than trimethyl isocyanurate towards alkalis, the former being scarcely affected, whereas the latter is converted even at  $40\text{--}45^{\circ}$  into *trimethylbiuret*,  $\text{C}_5\text{H}_{11}\text{N}_3\text{O}_2$ , which crystallises in slender needles and melts at  $126^{\circ}$  (corr.) Again, salicylamide,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ , is much less readily attacked than methylsalicylamide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH}_2$ , and, similarly, methylic salicylate is more resistant than methylic methylsalicylate,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COOMe}$ . Analogous results have been obtained with methylic parahydroxybenzoate and methylic anisate; ethylic acetoacetate and ethylic dimethylacetoacetate; hippuric acid,  $\text{NHBz} \cdot \text{CH}_2 \cdot \text{COOH}$ , and benzoylmethylamide,  $\text{NHMeBz}$ , and potassium cyanide and acetonitrile. A similar difference in behaviour is also exhibited by certain compounds towards potassium hydrosulphide; trichloropurine, for example, not being affected by this reagent, whilst 7-methyltrichloropurine is converted by it into thiochloropurine. No direct relation has been ascertained between this phenomenon and the heats of formation of the various substances concerned. It is to be noted that the compounds which offer the greatest resistance to alkalis are acid substances, and as such become electrolytically dis-



sociated in solution, and it seems possible that the complex negative ions thus formed may exert an electrical repulsion on the similarly charged hydroxyl ions which in some way hinders the chemical action.

A. H.

**Mercurydimethyl.** By EUGEN BAMBERGER (*Chem. Centr.*, 1898, ii, 1015; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 385—386).—By the action of nitric peroxide on mercurydimethyl, an extremely unstable acid,  $C_2H_5N_3O_4$ , which crystallises in white needles and melts at  $65-70^\circ$ , is obtained. On decomposition, it yields formic acid, carbonic anhydride, nitrous oxide, nitrogen, ammonia, and hydroxylamine, with some carbonic oxide and formaldehyde. According to the author, the acid is probably the *dioxime of imidocarbonic acid*,  $NH[C(OH):N\cdot OH]_2$ .

E. W. W.

**1:1-Dimethyltrimethylene.** By GABRIEL GUSTAVSON and (Miss) O. POPPER (*J. pr. Chem.*, 1898, [ii], 50, 458—461).—*Pentaglycol bromide*,  $CMe_2(CH_2Br)_2$ , obtained by the action of phosphorus tribromide on pentaglycol, boils at  $185-190^\circ$  at atmospheric pressure, and when treated with zinc dust in alcoholic solution, yields 1:1-dimethyltrimethylene,  $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CMe_2$ , boiling at  $21^\circ$ . This has a slight odour re-

sembling that of naphtha; a sp. gr. =  $0.6604$  at  $20^\circ/4^\circ$ ; and a refractive index =  $1.3659$ ; it is fairly stable towards potassium permanganate, but combines readily with bromine in the cold. That the substance has the above constitution, and is not isopropylethylene, is shown by the facts that it combines with hydriodic acid to form dimethylethylcarbinylic iodide, that its bromine compound,  $C_5H_{10}Br_2$ , when reduced, does not give the original hydrocarbon, but trimethylethylene, and that it dissolves in dilute sulphuric acid, whereas isopropylethylene does not.

The ease with which the hydrocarbon unites with bromine is not contradictory to the above formula, when it is remembered that the corresponding acid,  $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > C(COOH)_2$ , is readily acted on by bromine and hydrobromic acid.

A. W. C.

**Chlorination of Benzene in Presence of Aluminium Chloride.** By A. MOUNEYRAT and CH. POURET (*Compt. rend.*, 1898, 127, 1025—1027. Compare this vol., i, 1).—Aluminium chloride has been shown to be a powerful chlorinating agent in the aliphatic series (*Abstr.*, 1898, i, 613), and the authors' experiments indicate that it plays the same part when applied to aromatic substances. One molecular proportion of chlorine is rapidly absorbed when passed into dry benzene mixed with 3 per cent. of aluminium chloride at  $50-55^\circ$ ; the product mainly consists of chlorobenzene together with a mixture of the three dichlorobenzenes and unaltered hydrocarbon. When the monochloro-derivative is chlorinated in a similar manner, paradichlorobenzene predominates in the product and is partially separated from its isomerides by cooling the mixture in ice; the mother liquor from the crystals of the para-compound yields, on fractionation, a further quantity of this substance and the meta-isomeride. The following chloro-derivatives are obtained when benzene or its mono- and di-chloro-

derivatives are further chlorinated in the presence of the same amount of aluminium chloride: the three trichlorobenzenes, a tetrachlorobenzene melting at 134° and boiling at 240°, pentachlorobenzene, and hexachlorobenzene.

G. T. M.

**Mixed Phenylic Ethylic Phosphates.** By ALBERT MOREL (*Compt. rend.*, 1898, 127, 1023—1025. Compare this vol., i, 29).—*Diphenylic ethylic phosphate*,  $\text{PO}(\text{OPh})_2 \cdot \text{OEt}$ , prepared by the action of ethylic dichlorophosphate on dry sodium phenoxide at 0°, is a colourless, highly refractive oil with a fish-like odour boiling at 250—263° under a pressure of 70 mm.; it decomposes when distilled under the ordinary pressure.

*Phenylic diethylic phosphate*,  $\text{PO}(\text{OEt})_2 \text{OPh}$ , produced by slowly adding diethylic chlorophosphate to dry sodium phenoxide cooled by ice, is an oil greatly resembling the preceding compound, but rather more volatile; it boils at 210—230° under a pressure of 70 mm.

G. T. M.

**Synthesis of Phenol from Acetylene.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 127, 908—911).—The author has made experiments with a view to define the conditions under which acetylene is converted into phenol, with intermediate formation of a sulphonic acid. Pure and dry acetylene is passed for about 18 hours through sulphuric acid containing about 30 per cent. of sulphuric anhydride. The liquid is then diluted and neutralised with potassium carbonate, and the potassium sulphate and a crystallisable sulphonate,  $\text{C}_2\text{H}_4\text{O}_2(\text{SO}_3\text{K})_2$ , are separated, partly by concentration, and finally by the addition of alcohol. The mother liquor contains an amorphous salt, which seems to be an isomeride of the crystallisable salt.

The amorphous salt is mixed with its own weight of potassium hydroxide, heated at 180—220° in an atmosphere of hydrogen for 20 minutes, allowed to cool, mixed with excess of dilute sulphuric acid, and distilled. The distillate contains phenol, and a larger quantity can be obtained by again heating the residue left in the retort with potassium hydroxide and again distilling. A third treatment also yields some more phenol, and the total quantity of the latter is considerable, when compared with the original quantity of acetylene. The phenol is formed by the action of the alkali on the sulphonate, and not during the action of the sulphuric acid on the acetylene (*Ann. Chim. Phys.*, [iv], 19, 432).

C. H. B.

**Derivatives of Guaiacol.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 949—950).—*Orthonitrophenylguaiacol*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , made by the action of orthobromonitrobenzene on potassium guaiacol, forms transparent, yellow, fasciculated needles; it melts at 55° and boils at 213° under a pressure of 10 mm.

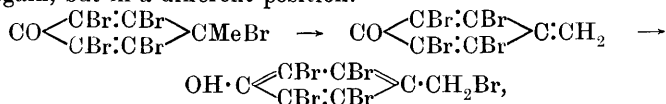
*Paranitrophenylguaiacol*,  $\text{C}_{13}\text{H}_{11}\text{NO}_4$ , forms beautiful, yellow needles, melts at 103·5—104°, and boils at 216° under a pressure of 10 mm.

*Picrylguaiacol*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$ , crystallises in yellow needles and melts at 117—118°.

*Methylenediguaiacol*,  $(\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_2\text{CH}_2$ , dissolves readily in the

ordinary media, with the exception of light petroleum, and forms beautiful, white crystals. It melts at  $79^{\circ}$ , and boils at  $217^{\circ}$  under 10 mm. pressure. A. L.

**Ketobromides and Methylenequinones.** By THEODOR ZINCKE (*J. pr. Chem.*, 1898, [ii], 58, 441—450).—The substances obtained by the action of bromine on alkylated phenols (ketobromides) contain the bromine atom next to the alkyl group, and in the author's opinion this is the cause of the active properties of these substances, as it allows of the elimination of the elements of hydrogen bromide, with formation of methylenequinones. This, however, does not readily account for the action of acid anhydrides, and it must be presumed that hydrogen bromide is first eliminated and then immediately taken up again, but in a different position.



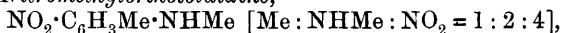
and then the anhydride reacts on this substance.

The ketobromides obtained from ortho- and para-cresol, xylol, pseudocumenol, and parethylphenol could not be converted into methylenequinone derivatives; but paradioxydiphenylmethane gives rise to benzylidenequinone. An outline of the results obtained is given, without however, any practical details. A. W. C.

**Alkyl Derivatives of Orthotoluidine.** By ROBERT GNEHM and E. BLUMER (*Annalen*, 1898, 304, 87—115).—According to Weinberg's observations, the monalkylic orthotoluidines behave as if the alkyl group wandered from the ortho-position to the amido-group. The authors' experiments indicate that the acetyl derivatives behave as if the methylicradicle occupied the para-position relatively to the amido-group. Attention has been drawn to the abnormal behaviour of these compounds by Rosenstiehl (compare Abstr., 1892, 1319), in the following terms. The methylic radicle in the ortho-position as regards nitrogen, imparts to secondary amines the properties of tertiary amines; to tertiary amines with free para-position the properties of an amine substituted in the para-position, and to a tertiary amine with a second amido-group in the para-position, the properties of an unsymmetrical alkylated diamine. The authors regard the first and second clauses of this rule as substantiated, but they cannot support the third. With the object of gaining information on this question, the following compounds have been examined.

Methylorthotoluidine *hydrochloride*, *hydrogen oxalate*, *oxalate*, and *picrate* are well-defined, crystalline salts (compare Scholl and Escales, Abstr., 1898, i, 182).

1 : 2 : 4-Nitromethylorthotoluidine,



is obtained by nitrating methylorthotoluidine, methylating 4-nitrotoluidine, or by hydrolysing the product of nitrating the acetyl derivative of methylorthotoluidine; it crystallises from alcohol in red, lustrous leaflets, and melts at  $107.5^{\circ}$ . The *hydrochloride* crystallises in leaflets, and the *picrate* in prisms; the *nitroso*-derivative crystallises in yellow

needles and melts at  $95^{\circ}$ , and the *acetyl* derivative melts at  $119^{\circ}$ . The *bromo-derivative* crystallises from petroleum in brownish-yellow needles, and melts at  $133^{\circ}$ . *Nitromethylorthotoluidine*, which may have the 1:2:3-constitution, is a by-product in the preparation of the 1:2:4 compound when 20 parts of sulphuric acid are employed in nitration; it melts at  $48^{\circ}$ .

*Orthonitro-orthotoluidineparasulphonic acid* [ $\text{Me}:\text{NH}_2:\text{NO}_2:\text{SO}_3\text{H}=1:2:3:5$ ], prepared by nitrating the product of sulphonation from orthacetotoluidide, crystallises from water in slender, yellow needles; hydrolysis yields 1:2:3-nitrotoluidine, which melts at  $95^{\circ}$ .

*Methyltolylenediamine* [ $\text{Me}:\text{NHMe}:\text{NH}_2=1:2:4$ ], obtained by reducing 1:2:4-nitromethylorthotoluidine with tin or zinc dust, is a colourless oil which boils at  $273^{\circ}$ , and forms a white, crystalline *sulphate*. Methyltolylene-blue forms a *hydrochloride*, which crystallises in leaflets with metallic lustre.

1:2:4-*Nitrodimethylorthotoluidine* [ $\text{Me}:\text{NMe}_2:\text{NO}_2=1:2:4$ ], prepared by nitrating dimethylorthotoluidine, forms the *hydrochloride*, which crystallises in yellow leaflets, and melts at  $192^{\circ}$ ; reduction converts it into 1:2:4-dimethyltolylenediamine, a yellow oil.

1:2:4-*Methylorthotoluidinesulphonic acid* [ $\text{Me}:\text{NHMe}:\text{SO}_3\text{H}=1:2:4$ ] crystallises from hot water in anhydrous leaflets soluble in water to the extent of 1.76 parts in 100 at  $15^{\circ}$ ; lead peroxide, in presence of acetic acid, develops an intense blue coloration, and fused potash converts it into an amidocresol. The *sodium* salt forms leaflets, and the *barium* salt, which is indistinctly crystalline, contains  $3\text{H}_2\text{O}$ . The *barium* salt of the *acetyl* derivative forms anhydrous prisms.

Another *methylorthotoluidinesulphonic acid*, prepared by heating methylorthotoluidine with 3 parts of sulphuric acid monhydrate at  $180$ – $210^{\circ}$  during 10 hours, crystallises in white, anhydrous needles, and develops a reddish-violet coloration with lead peroxide.

*Dimethyldiamidodi-orthotolylmethane*,  $\text{CH}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{NHMe})_2$ , produced on passing hydrogen chloride into formaldehyde mixed with methylorthotoluidine (2 mols.), crystallises from water in reddish-violet leaflets, and melts at  $87^{\circ}$ . M. O. F.

**Chlorophenetidines, Bromophenetidines, and Nitrophenetidines, and Azo-colouring Matters derived therefrom.** By FRÉDÉRIC REVERDIN and FRANZ DÜRING (*Ber.*, 1899, 32, 152–167).—With the purpose of gaining further information relative to the influence of substituent radicles on the shade of the colouring matters derived from diazotisable amines, the authors have prepared the following derivatives of phenetidine.

*Parachlororthamidophenetol* [ $\text{OEt}:\text{NH}_2:\text{Cl}=1:2:4$ ], obtained on reducing orthonitroparachlorophenetol with stannous chloride and hydrochloric acid, melts at  $42^{\circ}$ , and is volatile in steam; it develops a bluish-green coloration with ferric chloride, and gives a yellowish-green precipitate with potassium dichromate. The *picrate* forms yellow, silky needles, and melts and decomposes at  $132.5^{\circ}$ ; the *sulphate* dissolves readily in alcohol and water, and the *acetyl* derivative crystallises from dilute alcohol in lustrous leaflets melting at  $110^{\circ}$ . The base is also obtained by treating acetorthamidophenetol

with sodium chlorate and hydrochloric acid in acetic acid solution, the product being subsequently hydrolysed.

*Dichloroparamidophenetoil*,  $C_8H_5ONCl_2$ , prepared by chlorinating phenacetin and hydrolysing the product with boiling, concentrated hydrochloric acid, crystallises from dilute alcohol in prisms, and melts at  $63.5-64.5^\circ$ ; the *acetyl* derivative, which is the direct product, crystallises from alcohol in white needles, and melts at  $162^\circ$ . The *sulphate* forms white leaflets, and the *picrate*, long, yellow needles, melting at  $149-150^\circ$ . *Orthochloroparaphenacetin* is a bye-product in the chlorination of phenacetin; it melts at  $132^\circ$ .

*Orthochloroparamidophenetoil* [ $OEt : Cl : NH_2 = 1 : 2 : 4$ ], obtained on reducing orthochloroparanitrophenetoil, crystallises from dilute alcohol in small, white needles, and melts at  $66^\circ$ ; the *picrate* and *acetyl* derivative (orthochloroparaphenacetin) melt at  $167-170^\circ$  and  $132^\circ$  respectively. Orthochloroparamidophenetoil is also produced by chlorinating phenacetin and hydrolysing the product (compare Hodurek, Abstr., 1897, i, 276).

*Parachlorometamidophenetoil* [ $OEt : NH_2 : Cl = 1 : 3 : 4$ ], prepared by reducing parachlorometanitrophenetoil with tin and hydrochloric acid, remains liquid at  $-12^\circ$ ; the *acetyl* derivative and *picrate* melt at  $106^\circ$  and  $111^\circ$  respectively.

*2:5-Chloronitrophenetoil*,  $OEt \cdot C_6H_3Cl \cdot NO_2$ , crystallises from petroleum in pale yellow needles, and melts at  $64^\circ$ . Reduction with tin and hydrochloric acid gives rise to a hydrochloride which is readily oxidised.

*Orthobromoparamidophenetoil* [ $OEt : Br : NH_2 = 1 : 2 : 4$ ] has been prepared by Hodurek (*loc. cit.*); the *picrate* melts at  $178-179^\circ$ .

*Parabromorthamidophenetoil* [ $OEt : NH_2 : Br = 1 : 2 : 4$ ], produced in the form of its *acetyl* derivative by the action of bromine and caustic soda on orthophenacetin, is very volatile in steam, and crystallises from dilute alcohol in white needles melting at  $53^\circ$ ; the *acetyl* derivative crystallises from 60 per cent. alcohol in lustrous leaflets, and melts at  $133^\circ$ , whilst the *picrate* melts and decomposes at  $135-137^\circ$ . Unlike orthobromoparamidophenetoil, it has no reducing action on alcoholic silver nitrate, and the *sulphate* dissolves in sulphuric acid.

When parabromophenetoil is treated with nitric acid (2 parts) of sp. gr. = 1.485, at  $-10^\circ$ , it is converted into Stadel's 2:4-bromonitrophenetoil, which melts at  $98^\circ$ ; this instance of the wandering of a bromine atom from the para- to the ortho-position under the influence of nitric acid is comparable with the behaviour of parabromanisole (Reverdin, Abstr., 1897, i, 27). Bye-products in this action are Körner's 2:4:6-bromodinitrophenol, Varda's tribromophenetoil, and an oil yielding parabromorthamidophenetoil on reduction.

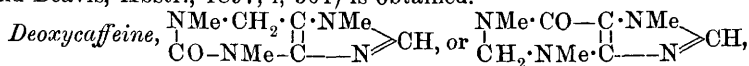
*Paramitro-orthamidophenetoil* [ $OEt : NH_2 : NO_2 = 1 : 2 : 4$ ], prepared by nitrating acetorthamidophenetoil (orthophenacetin) and hydrolysing the product, crystallises from dilute alcohol in orange needles or yellow leaflets, and melts at  $97^\circ$ ; the *acetyl* derivative melts at  $196^\circ$ .

*Metanitro-orthamidophenetoil* [ $OEt : NH_2 : NO_2 = 1 : 2 : 5$ ] is obtained in the form of its *acetyl* derivative when the operation is carried out at  $25-40^\circ$  instead of at  $0^\circ$ ; it crystallises from dilute alcohol in deep yellow needles, and melts at  $90^\circ$ . The *acetyl* derivative melts at  $165^\circ$ .

A supplement to the paper contains a report supplied by the Höchst Colour Works on the character of certain dyes, to which the foregoing bases give rise. M. O. F.

**Reduction of Acylamines to Alkylamines.** By THOMAS B. BAILLIE and JULIUS TAFEL (*Ber.*, 1899, 32, 68—77).—The oxygen atom of a carbonyl group to which an amido-group is attached, can, in many cases, be replaced by hydrogen by electrolytic reduction in strong sulphuric acid solution. In this way, benzamide, benzodimethylamide, acetanilide, acetorthotoluidide, acetyltetrahydroquinoline, and benzoylpiperidine have been respectively reduced to benzylamine, benzyltrimethylamine, ethylaniline, ethylorthotoluidine, ethyltetrahydroquinoline boiling at 256—258°, and benzylpiperidine. In some cases, the yields are good, in others poor, and in most cases the best conditions for the reduction have not been worked out.

When succanil (10 grams) is dissolved in concentrated sulphuric acid (90 grams) and water (10 grams), and electrolysed at 50° with a current of 5 ampères for 9 hours, 40 per cent. sulphuric acid being employed at the anode, a good yield of phenylpyrrolidone (Anschutz and Beavis, *Abstr.*, 1897, i, 364) is obtained.



is obtained when caffeine (1 part) dissolved in sulphuric acid (2·5 parts) and water (2·5 parts), is electrolysed with lead electrodes and a current of 15 ampères, 50 per cent. sulphuric acid being employed at the anode, and the temperature kept at 20—30°; the product of reduction is poured into water, neutralised with lime, filtered, evaporated under reduced pressure, and extracted with chloroform, the deoxycaffeine being deposited when the chloroform is evaporated. It is freed from caffeine by dissolving it in hydrochloric acid, extracting this solution several times with chloroform to remove caffeine, rendering alkaline, and again extracting with chloroform, finally crystallising the product from ethylic acetate. It crystallises with 1H<sub>2</sub>O, melts at 118° or, when anhydrous, at 147—148°, distils undecomposed at 245—248° under a pressure of 15—16 mm., and dissolves readily in cold alcohol, water, chloroform, or acetone. It is readily oxidised by sulphuric acid, but not by Fehling's solution, and its aqueous solution decolorises potassium permanganate and readily absorbs bromine. The *hydrochloride*, C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>O + HCl; *mercurichloride*, C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>O + 2HgCl<sub>2</sub>; *platinochloride*, and *picrate*, C<sub>14</sub>H<sub>15</sub>N<sub>7</sub>O<sub>8</sub>, melting and decomposing at 194—195°, have been prepared. Acetamide, acetylpiperidine, and 2-methylpyrrolidone could not be reduced by this process.

J. J. S.

**Nitrosoacylamines.** By CARL PAAL and H. APITZSCH (*Ber.*, 1899, 32, 78—80).—*Benzylnitrosoacetamide*, CH<sub>2</sub>PhAc·NO, is obtained when gaseous nitrous acid is passed into a solution of pure benzylacetamide in a small quantity of acetic acid; it is extracted with ether, and then forms a thick oil, which has not been obtained in a crystalline form. Boiling absolute alcohol decomposes it but slowly, the decomposition being more vigorous in the presence of potassium carbonate, with

formation of benzylic ethylic ether boiling at  $185^{\circ}$ , mixed with a small quantity of an ethereal salt of benzoic acid. Normal propylic alcohol also decomposes it in the presence of potassium carbonate, yielding benzylic propylic ether boiling at  $196^{\circ}$ .

Allylamine readily reacts on the nitrosamide, yielding benzylallylamine, together with other more complex compounds. J. J. S.

**Non-existence of Four Phenylparatolylmethenylamidines.** By HENRY L. WHEELER and T. B. JOHNSON (*Amer. Chem. J.*, 1898, 20, 853—861).—The preparation of phenylparatolylmethenylamine by four methods has been described by Walther (Abstr., 1897, i, 242), and by the latter in conjunction with Zwingenberger (Abstr., 1898, i, 519), each method apparently giving rise to a different product. One of the authors has previously shown, however, that only one phenylparatolylmethenylamine exists (Abstr., 1897, i, 465); it is now proved conclusively that Walther and Zwingenberger's product, melting at  $120^{\circ}$ , prepared from paratoluidine and diphenylmethenylamine, contained a considerable quantity of the latter in an unchanged state, and that their fourth product, melting at  $132^{\circ}$ , contained unchanged diparatolylmethenylamine. In the case of the modifications described as melting at  $98^{\circ}$  and  $102^{\circ}$ , prepared respectively from formoparatoluidide and formanilide, Walther has assumed that the methods of formation indicate their structure, although von Pechmann has frequently pointed out that such arguments are invalid in dealing with amidines. An attempt made by the authors to prepare by Walther's method the substance melting at  $98^{\circ}$  gave a product which, after seven crystallisations from light petroleum, did not melt above  $86^{\circ}$ ; an attempt to prepare the variety melting at  $102^{\circ}$  gave a product which melted at  $134$ — $135^{\circ}$ , and apparently consisted of diparatolylmethenylamine. From the above experiments, it is concluded that, without exception, the four products obtained by Walther are merely mixtures; pure phenylparatolylmethenylamine is stated to melt at  $86^{\circ}$ .

Phenylmethenylmethenylamidophenylidene,  $\text{NMePh}\cdot\text{CH}\cdot\text{NPh}$  (Comstock and Wheeler, Abstr., 1892, 705), is formed on adding a mixture of methylaniline and formanilide, in molecular proportion, to an excess of phosphorus trichloride, and also by the action of methylic iodide on diphenylmethenylamine, although in the latter case the yield is poor; it is a pale yellow oil which does not solidify at  $15^{\circ}$ , and boils at  $218.5$ — $219^{\circ}$  under a pressure of 26 mm. The *hydrochloride*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\cdot\text{HCl}$ , prepared by passing dry hydrogen chloride into a petroleum solution of the base, crystallises from absolute alcohol in large, transparent rhombohedra; the *aurichloride*,  $\text{C}_{14}\text{H}_{14}\text{N}_2\cdot\text{HAuCl}_4$ , separates from its alcoholic solution, on adding water, in yellow six-sided plates and melts at  $145^{\circ}$ . W. A. D.

**Electrolytic Preparation of Phenyl- $\beta$ -hydroxylamine.** By FRITZ HABER (*Zeit. Elektrochem.*, 1898, 5, 77—78).—A solution of nitrobenzene (20 grams) in glacial acetic acid (430 c.c.) diluted to 850 c.c. is used in the cathode compartment and dilute sulphuric acid in the anode compartment, a current of 4 ampères being employed with a cathode having 50 square cm. of surface. A suitable form of

apparatus with special cooling arrangements is described. About 7 grams of nitrobenzene yields 0.5 to 0.7 gram of phenyl- $\beta$ -hydroxylamine. Orthotolylhydroxylamine can be obtained in a similar way from orthonitrotoluene. T. E.

**Alphylhydroxylamines.** By EUGEN BAMBERGER (*Chem. Centr.*, 1898, ii, 1013; *from Arch. Sci. phys. nat. Genève*, [iv], 3, 386—387).—By the action of air and water, alphylhydroxylamines are converted into azoxy-compounds with formation of hydrogen peroxide, and these compounds can also effect the oxidation of indigo-carmin in presence of air. When diazomethane acts on phenylhydroxylamine, the latter behaves like a mixture of methylene and nitrogen, and *methylenediphenylhydroxylamine*,  $\text{CH}_2(\text{NPh}\cdot\text{OH})_2$ , nitrogen, and hydrogen are formed; the hydrogen reduces a part of the phenylhydroxylamine to aniline.

E. W. W.

**Electrolytic Reduction of Aromatic Nitro-compounds to Azo- and Hydrazo-compounds.** By KARL ELBS and OTTO KOPP (*Zeit. Elektrochem.*, 1898, 5, 108—113).—Within a porous pot, standing in a tall beaker, is placed an anode of platinum foil, and round it a cylinder of nickel wire gauze. The porous pot is filled with a cold saturated solution of sodium carbonate, and the solution to be reduced is poured hot into the annular cathode space where the passage of the current causes it to boil. Under these conditions, nitro-compounds are reduced very rapidly to azo-compounds, the completion of the reaction being indicated by evolution of hydrogen. The further reduction to hydrazo-compounds goes on more slowly, and best with a smaller current density. The current density (in ampères per square decimetre) calculated on the area of one side of the gauze cathode taken as though it were continuous, varies from 10 to 16 for the azo-compounds and from 2 to 3 for the hydrazo-compounds. The cathode solution contains sodium acetate (5 grams), 70 per cent. alcohol (200 c.c.), and from 10 to 20 grams of the nitro-compound; the yields are usually from 80 to 95 per cent. of the theoretical amount. The following compounds have been reduced: nitrobenzene, orthonitrotoluene, paranitrotoluene, paranitrorho-xylene, and metanitriline. A number of determinations of the current densities at which hydrogen begins to be evolved in solutions of nitro-compounds of different concentrations and at different temperatures are given; these values increase with rise of temperature and increase of concentration. T. E.

**Electrolytic Reduction of Metanitroparatoluidine.** By KARL ELBS and B. SCHWARZ (*Zeit. Elektrochem.*, 1898, 5, 113—115).—Metanitroparatoluidine is reduced to metadiamidoazotoluene under conditions similar to those described by Elbs and Kopp (preceding abstract). The current density must not exceed 4 to 5, otherwise metatolylenediamine is formed. The azo-compound is usually obtained in orange needles melting at 142—145°. Sometimes, however, it melts at 132° to 133°, or at 157° to 158°. The products of lower melting point are converted into those of higher melting point by treatment with concentrated sulphuric acid. The substances with the melting points 132—133° and 157—158° both crystallise in two different forms. Possibly, the



products of lower melting point are labile forms of the same substance. Metadiamidorthohydrazotoluene is obtained by reduction of the azo-compound, the yield being 40—50 per cent.; the low yield is due to the formation of metatolylenediamine, which may be obtained by distilling the solution from which the sparingly soluble hydrazo-compound has crystallised. By boiling the hydrazo-compound with an alcoholic solution of hydrochloric acid containing some sulphurous anhydride, it is converted into diamidotolidine; the free base, which forms colourless crystals melting at  $176^{\circ}$ , is but slightly affected by exposure to air and light. T. E.

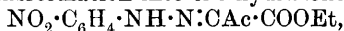
**Isodiazocompounds and their Compounds with Ethylic Acetoacetate.** By CARL BÜLOW (*Ber.*, 1898, 31, 3122—3131).—Isodiazocompounds (nitrosamines) are supposed not to enter into direct union with a methylene group which is combined with such groups as  $\text{NO}_2$ , CO, COOH, or COOEt. Paranitrisodiazobenzene, isodiazobenzene-parasulphonic acid, &c., do, however, so unite with ethylic acetoacetate, and that in alkaline solution, in which transformation into the normal diazo-compounds is impossible; the products are identical with those obtained from ethylic acetoacetate and the diazonium salts in acetic acid solution.

Paranitrisodiazobenzenesodium (nitrosamine red, paranitrophenyl-nitrosaminesodium) mixed with ethylic acetoacetate in dilute aqueous solution made feebly alkaline with sodium carbonate or hydroxide, gives a plentiful yield of Kjellin's ethylic paranitrobenzeneazoacetoacetate (*Abstr.*, 1897, i, 616),  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CHAc} \cdot \text{COOEt}$  [the author terms this ethylic paranitranitrilineazoacetoacetate, and gives similar names to the other compounds described in this paper] after remaining for 5 hours at the ordinary temperature, and by passing carbonic anhydride into the mother liquor until the latter is but just alkaline, a further crop of crystals can be obtained. This substance is not changed when it is boiled with acetic anhydride. When it is allowed to remain with dilute, aqueous-alcoholic sodium hydroxide, violet crystals of the *disodium* salt,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CNaAc} \cdot \text{COONa}$ , are deposited; these are very unstable, decomposing spontaneously into the *monosodium* salt; the same change occurs more readily on dissolving in water, with or without the addition of carbonic anhydride. When the disodium salt is dissolved in acetic acid, *paranitrobenzene-azacetoacetic acid* is formed; this is yellow, and melts and decomposes at  $217^{\circ}$ .

*Paranitrobenzeneazoacetoacetamide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CHAc} \cdot \text{CO} \cdot \text{NH}_2$ , is obtained by dissolving the ethylic salt in hot, alcoholic ammonia and allowing the solution to remain; it is yellow and melts at  $225$ — $226^{\circ}$ ; with methylamine instead of ammonia, a yellow *methylamide* melting at  $189^{\circ}$  is obtained. When the ethylic salt is left in contact with phenylhydrazine in alcoholic solution, some of the *phenylhydrazone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH}(\text{COOEt}) \cdot \text{CMe} \cdot \text{N} \cdot \text{NHPh}$ , is formed, but much of it is converted into 1-phenyl-3-methyl-4-paranitrobenzeneazo-5-pyrazolone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe} \cdot \text{N} \\ \diagup \\ \text{CO} - \text{NPh} \end{smallmatrix}$ . This can be prepared by boiling the mixed substances with alcohol and acetic acid; it melts at  $199.5^{\circ}$ ,

has a bluish lustre, dissolves in caustic alkalis, and is not decomposed by boiling with dilute acids. When it is nitrated at 55° with concentrated nitric acid and just enough water to prevent the separation of a crystalline salt, it yields 1-*paranitrophenyl*-3-methyl-4-*paranitrobenzene*-

azo-5-pyrazolone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{CH} \begin{smallmatrix} \text{CMe:N} \\ \text{CO-N} \end{smallmatrix} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ; this is yellow, melts above 280°, and explodes when heated quickly on platinum foil. It is also formed, in addition to *paranitrobenzene*azo-acetoacetic acid, when the ethylic salt of this acid is boiled with 10 per cent. hydrochloric acid for 30 hours; presumably part of the ethylic salt undergoes a transformation into the hydrazone,



from which *paranitrophenyl*hydrazine is then eliminated; this finally reacts with unchanged ethylic salt, forming the dinitropyrazolone.

C. F. B.

**Some Oxyazo-compounds.** By MAX KRAUSE (*Ber.*, 1899, 32, 124—127).—*Paramethoxybenzeneazophenol*,  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , prepared by the action of *paradiazoisol* chloride on an alkaline solution of phenol, crystallises from dilute acetic acid in glistening, red scales, which become orange-yellow when heated to 110°, and melt at 142°; it dissolves readily in acetic acid and benzene, and less readily in chloroform. By the action of *diazobenzene* chloride, it is converted into *benzeneazoparamethoxybenzeneazophenol* [ $\text{OH} : \text{N}_2\text{Ph} : \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} = 1 : 2 : 4$ ]; this crystallises from dilute acetic acid in glistening, chocolate-brown needles, and melts at 117°; it dissolves readily in ether, benzene, and acetic acid, less readily in light petroleum, xylene, and chloroform, and only slightly in alcohol.

*Benzeneazoparethoxybenzeneazophenol*, prepared in a similar way from *paradiazophenetol*, crystallises from dilute acetic acid in brownish-yellow needles and melts at 142°.

*Orthomethoxybenzeneazophenol*, from *orthodiazoisol*, separates from dilute acetic acid in splendid, brownish-yellow, glistening crystals, and melts at 146—147°; it is readily soluble in ether, alcohol, acetic acid, benzene, xylene, chloroform, and light petroleum. By the action of *diazobenzene* chloride, it is converted entirely into resinous products, as is also the corresponding ethoxy-compound.

*Parachlororthobenzeneazophenol*, [ $\text{OH} : \text{N}_2\text{Ph} : \text{Cl} = 1 : 3 : 4$ ], prepared by the action of *diazobenzene* chloride on an alkaline solution of *parachlorophenol*, crystallises from hot dilute acetic acid in fine, reddish-yellow needles melting at 110—111°; it dissolves readily in ether, alcohol, acetic acid, benzene, xylene, chloroform, and light petroleum.

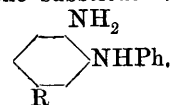
The chief product of the action of nitrosobenzene on *orthamidophenol* is triphenodioxazine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{O} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$ , and no large amount of *orthobenzeneazophenol* is produced.

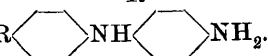
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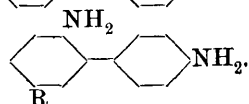
**Transformation of Hydrazo-compounds Substituted in the Para-position.** By PAUL JACOBSON (*Annalen*, 1898, 303, 290—305).—It has been observed by the author that, in the case of hydrazo-compounds which are substituted in the para-position, the nature of

the substituent exerts a marked influence on the course of the semidine transformation (Abstr., 1893, i, 330).

When a derivative of azobenzene having one substituent in the para-position is reduced with tin and hydrochloric acid, or the hydrazo-compound formed is first isolated and then treated with acid stannous chloride, the following changes may occur. (1) Simple transformation into benzidine with elimination of the substituent.

(2) Transformation into an orthosemidine base, 

(3) Transformation into a parasemidine base, 

(4) Transformation into a diphenyl base, 

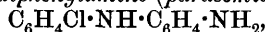
(5) Resolution into aniline and a para-substituted aniline.

These five changes can occur simultaneously, as in the case of parachlorhydrazobenzene, which yields benzidine, aniline, parachloraniline, chlorodiamidodiphenyl, and the ortho- and para-semidine bases (following abstract); or one product preponderates, the others occurring as bye-products.

The effects of the substituents Cl, Br, I, OEt, OAc, NMe<sub>2</sub>, NHAc, Me, and COOH have now been studied (succeeding abstracts) and submitted to comparison and discussion. M. O. F.

**Transformation of Parachlorhydrazobenzene.** By PAUL JACOBSON and HERMANN STRÜBE (*Annalen*, 1898, 303, 305—319).—As already stated (preceding abstract), when parachlorhydrazobenzene is subjected to the influence of stannous chloride and hydrochloric acid, the five possible changes occur simultaneously.

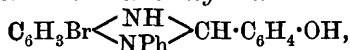
*Parachloroparamidodiphenylamine (parasemidine base),*



was obtained synthetically from diphenylamine, for comparison with one of the products of reducing parachlorhydrazobenzene, with which it was found to be identical; it crystallises from petroleum in colourless leaflets, and melts at 71°. The *salicylidene* and *benzylidene* derivatives melt at 170° and 144° respectively; the *acetyl* and *diformyl* derivatives at 207° and 103° respectively, and the *thiocarbamide*, which crystallises from alcohol in lustrous leaflets, melts at 176°. 5:2:4'-*Chlorodiamidodiphenyl*, NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Cl·C<sub>6</sub>H<sub>4</sub>·NH<sub>2</sub>, is obtained in a purified form from the *disalicylidene* derivative, which crystallises from alcohol in needles, and melts at 166—167°; the *diacetyl* and *diformyl* derivatives melt at 204° and 194° respectively, and the *dibenzylidene* derivative melts at 104°. M. O. F.

**Transformation of Parabromhydrazobenzene.** By PAUL JACOBSON and RUDOLF GROSSE (*Annalen*, 1898, 303, 319—330).—2:5-*Amidobromodiphenylamine (orthosemidine base)*, NH<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>Br·NHPh, constitutes 12—15 per cent. of the product from parabromhydrazobenzene and stannous chloride; it crystallises from benzene on adding

petroleum in colourless needles, which melt at  $106^{\circ}$  and become greyish-violet when exposed to air. When ferric chloride is added to a dilute solution of the *hydrochloride*, the liquid becomes red, and then violet, precipitating microscopic, indigo blue needles having copper reflex. The orthosemidine base is also obtained by reducing 5 : 2-bromonitrodiphenylamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NHPh}$ , which crystallises from hot alcohol in reddish-brown needles and melts at  $116^{\circ}$ . The *azimide*,  $\text{C}_6\text{H}_3\text{Br} \langle \text{---N} \rangle_{\text{NPh}}$ , separates from petroleum in silky, greyish-violet needles and melts at  $126^{\circ}$ . The *salicylidene* derivative,



crystallises from alcohol in lustrous, sulphur-yellow needles and melts at  $155^{\circ}$ , and the *methenyl* derivative,  $\text{C}_6\text{H}_3\text{Br} \langle \text{---N} \rangle_{\text{NPh}} \text{CH}$ , in white needles which rapidly become violet; it melts at  $110^{\circ}$ .

5 : 2 : 4'-Bromodiamidodiphenyl,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , produced to the extent of 20—25 per cent. by the transformation of parabromhydrazobenzene, yields the *salicylidene* derivative,  $\text{C}_{26}\text{H}_{19}\text{N}_2\text{O}_2\text{Br}$ , which crystallises from petroleum and melts at  $154$ — $156^{\circ}$ ; the *diacetyl* and *diformyl* derivatives melt at  $223^{\circ}$  and  $191^{\circ}$  respectively.

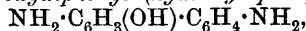
*Parabromoparamidodiphenylamine*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , forms lustrous leaflets and melts at  $79^{\circ}$ . M. O. F.

**Transformation of Pariodohydrazobenzene.** By PAUL JACOBSON, F. K. FERTSCH, and FRITZ HEUBACH (*Annalen*, 1898, 303, 330—340). —5 : 2 : 4'-Iododiamidodiphenyl,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{I} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , obtained by the transformation of pariodohydrazobenzene with stannous chloride, yields the *dihydrochloride* in long, lustrous needles. The *salicylidene* derivative melts at  $151^{\circ}$ , and the *paranitrobenzylidene* derivative crystallises from benzene in yellow needles and melts at  $213^{\circ}$ .

2 : 5 : 4'-Tri-iododiphenyl,  $\text{C}_6\text{H}_4\text{I} \cdot \text{C}_6\text{H}_3\text{I}_2$ , prepared by the action of potassium iodide on diazotised iododiamidodiphenyl, separates from alcohol in brownish crystals and melts at  $124$ — $125^{\circ}$ ; when heated with zinc dust in an atmosphere of hydrogen, it yields diphenyl.

5 : 2-Iodoamidodiphenylamine (*orthosemidine base*),  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{NHPh}$ , forms with benzil the *stilbazonium base*, of which the *hydrochloride* crystallises from alcohol in yellow needles; the *methenyl* compound forms white needles and melts at  $161^{\circ}$ . The base is identical with the product obtained by reducing 5 : 2-iodonitrodiphenylamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{I} \cdot \text{NHPh}$ , which crystallises from alcohol in carmine-red needles, and melts at  $111^{\circ}$ . M. O. F.

**Transformation of Paracetoxyhydrazobenzene.** By PAUL JACOBSON and HERMANN TIGGES (*Annalen*, 1898, 303, 341—352). —2 : 4' : 5-Diamidohydroxydiphenyl (*hydroxydiphenylene*),



is the chief product of the action of stannous chloride on paracetoxyhydrazobenzene in presence of hydrochloric acid; it crystallises from benzene in slender needles which quickly become coloured, and melts at  $148^{\circ}$ . This base forms the active constituent of the photographic developer "diphenal." The *salicylidene* derivative forms lustrous,

yellowish-brown leaflets and melts at  $206-237^{\circ}$ ; the *anisylidene* derivative melts at  $184-185^{\circ}$ , and the *paranitrobenzylidene* derivative forms an orange powder which melts at  $218^{\circ}$ . The *diformyl* and *diacetyl* derivatives melt at  $243^{\circ}$  and  $269^{\circ}$  respectively, and the *tribenzoyl* derivative crystallises from dilute alcohol in microscopic needles, and melts at  $177-178^{\circ}$ .

*Dianisylidene-ethoxydiphenylene*,  $C_{30}H_{28}N_2O_3$ , obtained by heating the anisylidene derivative with ethylic bromide and sodium ethoxide, crystallises from alcohol in yellow needles, and melts at  $124^{\circ}$ . *Diacetyl-ethoxydiphenylene*,  $C_{18}H_{20}N_2O_3$ , is prepared by the same method from the diacetyl derivative of diamidohydroxydiphenyl, and melts at  $190-191^{\circ}$ .

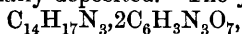
*Ethoxydiphenylene* (2 : 4' : 5-diamidoethoxydiphenyl),



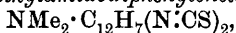
produced on hydrolysing the two foregoing substances with dilute sulphuric acid and alcoholic potash respectively, crystallises from dilute alcohol in nacreous leaflets and melts at  $97^{\circ}$ . The *hydrochloride* forms white needles, and the *dibenzoyl* derivative melts at  $221^{\circ}$ .

M. O. F.

**Transformation of Paradimethylamidohydrazobenzene.** By PAUL JACOBSON and R. KUNZ (*Annalen*, 1898, 303, 353—361. Compare Boyd, *Trans.*, 1894, 65, 879). — *Dimethyltriamidodiphenyl*,  $C_{12}H_7(NH_2)_2 \cdot NMe_2$  [= 2 : 4' : 5], is the chief product of the transformation of paradimethylamidohydrazobenzene, and melts at  $87-89^{\circ}$ ; on adding ferric chloride to an aqueous solution of the base, an intense violet coloration is developed, rapidly becoming dark blue, and if hydrochloric acid is then added to the liquid, it becomes green, and a blue precipitate is gradually deposited. The yellow *picrate*,



forms yellow, prismatic crystals and melts at  $127^{\circ}$ ; aqueous ammonia converts this salt into the brown *picrate*,  $C_{14}H_{17}N_3 \cdot C_6H_3N_3O_7$ , which crystallises from water in reddish-brown needles and melts at  $175^{\circ}$ . The *diacetyl* derivative crystallises from dilute alcohol in small, white needles and melts at  $233^{\circ}$ . The *dibenzylidene* and *disalicylidene* derivatives melt at  $146-147^{\circ}$  and  $158-159^{\circ}$  respectively. The *thiophosgene* derivative (*dimethylamidodiphenylenethiocarbimide*),

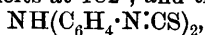


crystallises from petroleum in yellow, prismatic needles, and melts at  $149^{\circ}$ ; the *thiourethane*,  $C_{18}H_{19}N_3OS_2$ , obtained by the action of boiling alcohol, melts at  $170^{\circ}$ .

M. O. F.

**Transformation of Paracetamidohydrazobenzene.** By PAUL JACOBSON and R. KUNZ (*Annalen*, 1898, 303, 362—367). — *Paramido-paracetamidodiphenylamine*,  $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NHAc$ , which constitutes 15 per cent. of the product from paracetamidohydrazobenzene and stannous chloride, melts at  $178^{\circ}$ , and crystallises from hot water in lustrous, white leaflets, which become red; hydrolysis converts it into the *paradiamidodiphenylamine* described by Nietzki. The latter base can also be obtained in one operation by treating acetamido-

hydrazobenzene with hydrochloric acid and stannous chloride; the *dibenzylidene* derivative melts at 182°, and the *thiocarbimide*,



melts at 170°.

M. O. F.

**Transformation of Paramethylhydrazobenzene.** By PAUL JACOBSON and W. LISCHKE (*Annalen*, 1898, 303, 367—383).—*Paramethylhydrazobenzene*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{NHPh}$ , obtained by reducing paramethylazobenzene with zinc dust and caustic soda, melts at 86—87°; and the *acetyl* and *diacetyl* derivatives at 140° and 91° respectively. The *phenylthiocarbimide* crystallises from alcohol in colourless, six-sided plates, and melts at 152°.

The orthosemidine base, produced by the transformation of paramethylhydrazobenzene, has not been obtained crystalline; the *methenyl* derivative,  $\text{C}_{14}\text{H}_{12}\text{N}_2$ , yields a *picrate* which melts at 195—198°, and a *mercurichloride*, which crystallises in microscopic needles and melts at 163—164°. These derivatives are identical with the compounds obtained from phenylorthotolylenediamine prepared by Schraube and Romig (*Abstr.*, 1893, i, 340). The isomeric base, *paratolylorthophenylenediamine*, has been recently described by O. Fischer (*Abstr.*, 1896, i, 628); the *methenyl* compound melts at 163—164°, and the *mercurichloride* at 160°. It follows that the crude base obtained by the transformation of paramethylhydrazobenzene contains the orthosemidine base, phenylorthotolylenediamine; the parasemidine base, paratolylparaphenylenediamine (Reichold), is also among the products.

M. O. F.

**Transformation of Hydrazobenzeneparacarboxylic Acid.** By PAUL JACOBSON and ADOLF STEINBRECK (*Annalen*, 1898, 303, 384—391).—The *methylic* and *ethylic* salts of azobenzenecarboxylic acid melt at 123—124° and 85—86° respectively. *Hydrazobenzeneparacarboxylic acid*,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , prepared by reducing azobenzeneparacarboxylic acid in alcoholic solution with zinc dust and glacial acetic acid, crystallises from dilute alcohol in white needles and melts at 192—193°; the *methylic* salt melts at 114—115°. Benzidine is the only product of the treatment with stannous chloride which has been hitherto isolated.

M. O. F.

**Symmetrical Dibenzylhydrazine.** By THEODOR CURTIUS and ERWIN QUEDENFELDT (*J. pr. Chem.*, 1898, [ii], 58, 369—392).—Some part of this work has already been noticed (*Abstr.*, 1896, i, 28). The colourless oil obtained by exposing dibenzylhydrazine to the air crystallises, to some extent, after a time, but the crystals show no constant melting point. The base can be preserved in an atmosphere of carbonic anhydride without undergoing change. Acetyldibenzylhydrazine cannot be further acetylated by heating with acetic anhydride in sealed tubes.

Dibenzylhydrazine is more strongly basic than hydrazobenzene, and does not suffer rearrangement when treated with concentrated mineral acids.

*Bis-azidiphenylmethane*,  $\text{CH}_2\text{Ph}\cdot\text{N}:\text{N}:\text{CH}_2\text{Ph}$ , obtained by the oxidation of  $\text{CH}_2\text{Ph}\cdot\text{N}:\text{N}:\text{CH}_2\text{Ph}$

tion of dibenzylhydrazine in alcoholic solution with mercuric oxide, crystallises from alcohol in beautiful, long needles melting at  $152^{\circ}$ , and is stable in presence of dilute acids or alkalis; concentrated alcoholic hydrogen chloride decomposes it into benzyldeneazine and dibenzylhydrazine hydrochloride.

When preparing benzyldeneazine tetrabromide, only about one-half of the theoretical yield is obtained. When kept, the filtered chloroform solution gives off hydrogen bromide, and when the chloroform has been evaporated, the red oily residue is found to consist of benzaldehyde and a compound,  $C_{17}H_{13}N_3$ , crystallising in large, colourless prisms melting at  $207^{\circ}$ ; towards acids, it behaves as a weak base.

Benzyldeneazine tetrabromide dissolves in alcohol with evolution of nitrogen, ethylic bromide being formed, and also a colourless, peculiar smelling oil boiling at  $50^{\circ}$  under a pressure of 15 mm., identical with the substance obtained from benzyldenic bromide and alcohol.

*Benzyldenic bromide*,  $CHPhBr_2$ , obtained by the action of phosphorus pentabromide on benzaldehyde, is a colourless, highly refractive oily liquid boiling at  $156^{\circ}$  under a pressure of 23 mm. It has a sp. gr. = 1.51 at  $15^{\circ}/15^{\circ}$  and refractive index = 1.541.

*Benzyldeneazine monhydrochloride*,  $CHPh \cdot N \cdot NCl \cdot CH_2Ph$ , prepared by the action of hydrogen chloride on an ethereal solution of the base, forms yellow flakes melting at  $150^{\circ}$ .

Chlorine unites directly with benzyldeneazine in chloroform solution, forming a compound crystallising from alcohol in needles melting at  $57^{\circ}$ , whilst iodine gives rise to a compound crystallising from alcohol in steel-blue needles melting at  $150^{\circ}$ .

A. W. C.

**Formation of Chains. XXXIII. Aromatic Monacid Bases and the Bromides of  $\alpha$ -Bromo-fatty Acids.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 3236—3240).—The bromides of  $\alpha$ -bromo-fatty acids react in the normal manner with primary and secondary aromatic amines, substituted anilides being formed. The propionyl derivatives melt at a higher temperature than the butyryl derivatives, and these again at a higher temperature than the isobutyryl derivatives, whilst these last melt at a lower temperature than the isovaleryl derivatives. The only exceptions to this rule are  $\alpha$ -bromisobutyrylmetatoluidide and the corresponding orthonitranilide, each of which melts at a higher temperature than the corresponding butyryl derivative.

The following new compounds have been prepared in the course of the investigation.

[With TSCHUNKEW.]— *$\alpha$ -Bromopropionylbenzylamide*, colourless needles melting at  $92^{\circ}$ ;  *$\alpha$ -bromobutyrylbenzylamide*, long needles melting at  $74^{\circ}$ ;  *$\alpha$ -bromisobutyrylbenzylamide*, needles melting at  $72^{\circ}$ ;  *$\alpha$ -bromisovalerylbenzylamide*, silky needles melting at  $98^{\circ}$ ;  *$\alpha$ -bromisovalerylamide*, colourless plates melting at  $133^{\circ}$ .

[With PÄPKE.]— *$\alpha$ -Bromisovalerylorthotoluidide*, stellate groups of needles melting at  $125^{\circ}$ ;  *$\alpha$ -bromopropionylmetatoluidide*, needles melting at  $80^{\circ}$ ;  *$\alpha$ -bromobutyrylmetatoluidide*, needles melting at  $79^{\circ}$ ;

*α*-bromisobutyrylmetatoluidide, needles melting at 91°; *α*-bromisovalerylmetatoluidide, needles melting at 135°; *α*-bromisovalerylparatoluidide, needles melting at 124°. *α*-Bromopropionylmetaxyldide, silky needles melting at 166°; *α*-bromobutyrylmetaxyldide, melting at 145°; *α*-bromisobutyrylmetaxyldide, melting at 103°; *α*-bromisobutyrylmetaxyldide, melting at 153°; *α*-bromisovaleryl-*α*-naphthalide, melting at 172°; *α*-bromisovaleryl-*β*-naphthalide, melting at 145°. *α*-Bromopropionyl-orthonitranilide, fascicular groups of needles melting at 62°; *α*-bromobutyrylorthonitranilide, needles melting at 47°; *α*-bromisobutyrylorthonitranilide, melting at 68°; *α*-bromisovalerylorthonitranilide, melting at 52.5°.

[With WATSCHJANZ.]—*α*-Bromopropionylmetanitranilide, prismatic needles melting at 137°; *α*-bromobutyrylmetanitranilide, melting at 99°; *α*-bromisobutyrylmetanitranilide, prisms melting at 99°; *α*-bromisovalerylmetanitranilide, prismatic needles melting at 107°.

[With HIRSCHFELD.]—*α*-Bromopropionylparanitranilide, rhombic tablets melting at 153°; *α*-bromobutyrylparanitranilide, short needles melting at 140°; *α*-bromisobutyrylparanitranilide, long needles melting at 123°; *α*-bromisovalerylparanitranilide, needles melting at 183°. *α*-Bromisovalerylmethylanilide has hitherto only been obtained as an oily liquid boiling at 160—163° under a pressure of 11 mm. A. H.

**Formation of Chains. XXXIV. Aromatic Diacid Bases and the Bromides of *α*-Bromo-fatty Acids.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 3241—3248. Compare the foregoing abstract).—Experiments on the introduction of brominated acid radicles into diacid aromatic bases have resulted in a general confirmation of the author's theory of dynamical collisions. Hydrazobenzene, as a rule, only admits of the introduction of a single acid radicle, but does not yield an acid derivative with *α*-bromisobutyric bromide, which has no hydrogen combined with the *α*-carbon atom. *α*-Bromopropionyl-diphenylhydrazide,  $\text{NHPh} \cdot \text{NPh} \cdot \text{CO} \cdot \text{CHBrMe}$ , crystallises in small needles melting at 137°; *α*-bromobutyryldiphenylhydrazide forms long, pointed needles melting at 123°; *α*-bromisovaleryldiphenylhydrazide crystallises in small, colourless tablets melting at 106°. When hydrazobenzene is treated with *α*-bromisobutyric bromide, it yields azobenzene and *α*-bromisobutyrylanilide.

[With SCHATZ.]—Methylenediphenylamine does not yield any acid derivatives, substituted anilides being obtained by the action of the *α*-bromo-bromides. *Methylenediparaphenetidine*,  $\text{CH}_2(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$ , which crystallises in silky needles melting at 80°, is converted by benzoic chloride into *benzoylphenetidide* melting at 173°, and by *α*-bromopropionic bromide into *bromopropionylphenetidide* melting at 138°.

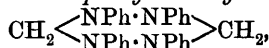
[With PÄPKE.]—Ethylenediphenyldiamine and the corresponding orthotolyl, paratolyl, and *β*-naphthyl derivatives permit of the introduction of two acid radicles, whereas the *α*-naphthyl derivative only reacts with one molecule of the acid bromide. *Di-α-monobromisovalerylethylenediphenyldiamine*,  $\text{C}_2\text{H}_4(\text{NPh} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHMe}_2)_2$ , crystallises in colourless needles melting at 147°. *Di-α-monobromisovalerylethylenediorthotolyldiamine* crystallises in small plates melting at



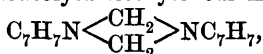
203°; the *paratolyl* compound melts at 109°, and the  $\beta$ -*naphthyl* compound at 193°.  $\alpha$ -*Bromisovaleryldi- $\alpha$ -naphthylethylenediamine*,  $\text{CHMe}_2 \cdot \text{CHBr} \cdot \text{CO} \cdot \text{N}(\text{C}_{10}\text{H}_7) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , melts at 223°.

[With TSCHUNKIEW.]—*Di- $\alpha$ -monobromisobutyryldi- $\beta$ -naphthylethylenediamine* crystallises in needles melting at 201°. *Diparatolyltrimethylenediamine*,  $\text{C}_3\text{H}_6(\text{NH} \cdot \text{C}_6\text{H}_4\text{Me})_2$ , crystallises in colourless, silvery plates melting at 73°, and readily yields diacid derivatives. The *dimono-bromopropionyl* compound melts at 127°, and the corresponding *isobutyryl* derivative at 113°. A. H.

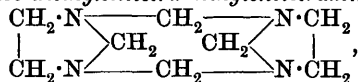
**Formation of Chains. XXXV. Formaldehyde and Diacid Bases.** By CARL A. BISCHOFF (*Ber.*, 1898, 31, 3248—3258).—Bases of the type of those employed in the experiments described in the foregoing paper were treated with formaldehyde, in order to ascertain what conditions are favourable to the formation of ring complexes containing 2 nitrogen atoms. It was found that polymeric substances are usually produced when rings containing 3 or 4 atoms might be expected, whereas rings containing 5 atoms are readily produced, and no reaction occurs in cases in which the formation of a 6-atom ring might be expected. Hydrazobenzene readily reacts with formaldehyde to produce *tetraphenyldimethylenetetrazine*,



which crystallises in colourless tablets and melts at 200°. Diphenylmethylenediamine reacts with the aldehyde to form trimethylenetri-aniline,  $\text{NPh} \begin{array}{c} \text{CH}_2 \cdot \text{NPh} \\ \text{CH}_2 \cdot \text{NPh} \end{array} \text{CH}_2$ , melting at 143°, accompanied by a compound which melts at 177—178° and is probably an isomeride or polymeride of the compound of low melting point. Three condensation products of formaldehyde with methylenediparatoluidine have been described; diparatolyldimethylenediamine,



melting at 90° (Löb, this vol., i, 123), a polymeride of this, melting at 127—128° (Eibner, *ibid.*, 41), and a third substance isomeric with the latter, melting at 225—227°; the last two compounds have the same molecular weight in boiling benzene solution, and are probably geometrical isomerides of the constitution  $\text{C}_7\text{H}_7 \cdot \text{N} \begin{array}{c} \text{CH}_2 \cdot \text{N}(\text{C}_7\text{H}_7) \\ \text{CH}_2 \cdot \text{N}(\text{C}_7\text{H}_7) \end{array} \text{CH}_2$ . Ethylenediamine reacts with formaldehyde to produce *diethylenetetramethylenetetramine*,



which crystallises in rhombic pyramids, melts at 196°, and boils at 250° with slight decomposition. Ethylenediphenylamine reacts with formaldehyde to produce *diphenyltetrahydroglyoxaline*,  $\text{NPh} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{NPh} \end{array}$ ,

which crystallises in small, colourless plates, and melts at 124°. *Diphenyldimethylethylenediamine*, melting at 165°, was not produced in the reaction, no methylation of the secondary base by the form-

aldehyde having taken place; this base can, however, readily be prepared by the action of monomethylaniline on ethylenic bromide. Nitric acid converts the glyoxaline derivative into *dinitrosodiphenylethylenediamine* melting at 157—158°. Diparethoxydiphenylethylenediamine, when treated with formaldehyde, yields *paradiethoxydiphenyltetrahydroglyoxaline*,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \end{smallmatrix}$ , which crystallises in colourless, silvery plates melting at 214°. Diparatolyltrimethylenediamine does not react with formaldehyde, and it was found impossible to synthesise any ring containing 2 atoms of nitrogen and 4 of carbon by the methods employed with the bases already discussed. *Malonylphenetidine*, melting at 226°, also gives no reaction with formaldehyde, whilst diparethoxydiphenylmethylenediamine is converted by formaldehyde into an open chain compound, *malonyldiphenetidine*,  $\text{CH}_2(\text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$ , melting at 226°. A. H.

**Condensation of Phthalimide with Formaldehyde.** By FRANZ SACHS (*Ber.*, 1898, 31, 3230—3235. Compare *Abstr.*, 1898, i, 475).—Phthalimide readily reacts with aqueous formaldehyde at 100° to form hydroxymethylphthalimide,  $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{N} \cdot \text{CH}_2 \cdot \text{OH}$ , which has previously been prepared from bromomethylphthalimide. This is converted by acetic anhydride into the *acetate*, which melts at 118°, and does not lose formaldehyde when heated. Other aldehydes do not form similar condensation products with phthalimide.

When phthalimide is brought into contact with formaldehyde and piperidine, condensation takes place, *phthalylpiperylmethylenediamine*,  $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{N} \cdot \text{CH}_2 \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH}_2$ , being formed; this is almost insoluble in water, crystallises in long needles, melts at 117—118°, yields a yellow, sparingly soluble *picrate*, and is readily decomposed by alkalis and acids. When an alcoholic solution of phthalimide is heated at 100° with formaldehyde and piperidine, the latter acts as a reducing agent, and methylphthalimide is formed; this reaction affords a means of preparing methylamine from ammonia and formaldehyde. Tetrahydroquinoline does not appear to act in the same way as piperidine, since no methylphthalimide is obtained, a vitreous mass of unknown constitution being produced. Aqueous aniline converts both hydroxymethylphthalimide and bromomethylphthalimide into *phthalylphenylmethylenediamine*,  $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{N} \cdot \text{CH}_2 \cdot \text{NHPh}$ , which crystallises in yellow, rectangular tablets; this is accompanied by a small amount of a white, sparingly soluble *substance* melting at 257°. Phenylhydrazine behaves in a similar manner to aniline, producing *phthalimidomethylenephénylhydrazine*,  $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{N} \cdot \text{CH}_2 \cdot \text{N}_2\text{H}_3\text{Ph}$ , which forms yellow needles melting at 120—121°. A. H.

**Weith's Polymeric Carbodiphenylimide.** By CARL SCHALL (*J. pr. Chem.*, 1898, [ii], 58, 461—464).—By acting on sulphocarbani-  
lide with boiling benzene, small amounts of triphenylguanidine and pentaphenylbiguanide are formed; after treating the partially solidified distillate with light petroleum, an oily di-imide is obtained, which solidifies when kept for some time. This substance, which shows the characteristics of Weith's polymeric carbodiphenylimide (this Jour.,

1876, ii, 419), melts at 168—170°, but no solvent could be found from which it could be crystallised. When heated, it is transformed into the oily *α*-carbodiphenylimide. *Acetylphenylhydrazoncarbodiphenylamine*,  $C_{21}H_{20}N_4O$ , prepared by heating a mixture of carbodiphenylimide and acetylphenylhydrazine, in molecular proportion, at 160—200°, crystallises from alcohol and melts at 157°. Alcoholic potash removes the acetyl group, giving rise to Marckwald and Wolff's (Abstr., 1893, i, 25) azo-base,  $NPh:N\cdot C(NHPh):NPh$ . Bromine produces a *tribromoderivative*,  $C_{21}H_{17}Br_3N_4O$ , which crystallises from glacial acetic acid and melts at 227°, with production of a red coloration.

Benzoylphenylhydrazine gives rise to the corresponding *benzoyl* derivative, separating from alcohol in white crystals melting at 110—111°. A. W. C.

**Derivatives of Metahydroxybenzaldehyde.** By MAX KRAUSE (*Ber.*, 1899, 32, 122—124. Compare Abstr., 1897, i, 53).—2:4:6-*Tribromometahydroxybenzaldehyde* crystallises from dilute acetic acid in yellowish-white needles and melts at 119°; the *oxime*, when crystallised from xylene or acetic acid, melts at 186°, but a small quantity of another substance melting at 226° is also produced; this appears to be an isomeric form. *Acetyl-2:4:6-tribromometahydroxybenzonitrile* separates from dilute alcohol in yellowish-white, glistening flakes, and melts at 156—158°, whilst 2:4:6-*tribromometahydroxybenzonitrile* separates from light petroleum in yellow needles and melts at 168°. 2:4:6-*Tribromometahydroxybenzoic acid* crystallises from hot water in long, glistening needles which have the composition  $2C_7H_3Br_3O_3 + H_2O$ : the anhydrous acid is insoluble in benzene and petroleum, slightly soluble in chloroform and xylene, and dissolves readily in alcohol, ether, and acetic acid; it melts at 146—147°, and is identical with the acid prepared by Werner (Abstr., 1886, 1015) by the direct bromination of metahydroxybenzoic acid; the *methylic* salt crystallises from light petroleum in flakes and needles, and melts at 119—121°.

2:4:6-*Trichlorometahydroxybenzaldehyde* crystallises from dilute acetic acid in colourless needles and melts at 115—116°; the *oxime* separates from dilute alcohol in glistening needles and melts at 170°; it dissolves readily in alcohol, ether, and acetic acid, but is only slightly soluble in benzene, xylene, chloroform, and light petroleum. *Acetyl-2:4:6-trichlorometahydroxybenzonitrile* separates from dilute acetic acid in glistening flakes and melts at 82—83°; 2:4:6-*trichlorometahydroxybenzonitrile* crystallises from alcohol in yellowish, glistening needles and melts at 157°. T. M. L.

**Dinitrophenyldiacetylmethane.** By FERNAND MUTTELET (*Bull. Soc. Chim.*, 1897, [iii], 17, 808—809).—The hydrogen atoms of the central  $CH_2$  group in acetylacetone can be replaced by aliphatic alkyl groups, and it was desired to ascertain whether the introduction of an aromatic radicle could be effected in a similar manner. For this purpose, 1:2:4-chlorodinitrobenzene, in which the chlorine atom possesses considerable mobility, was added to an equal weight of sodium acetylacetone dissolved in hot alcohol, and the liquid subsequently poured into water; the oily liquid which separated was soon

converted, by agitation, into a mass of crystals melting at  $121^{\circ}$ , and only slightly soluble in cold alcohol. The crystals did not lose weight when heated at  $100^{\circ}$ , and yielded analytical results corresponding with the formula  $\text{CHAc}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$ . The study of this compound will be continued. N. L.

**Solubility of the Nitrobenzoic Acids. II.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, 17, 329—334. Compare this vol., i, 141).—The author has previously shown that, although the solubilities of mixtures of paranitrobenzoic acid with the ortho- and with the meta-acid are those foreseen by theory, the same is not true of the solubility of a mixture of the ortho- and meta-acids; but assuming that a change in the solid phase occurs when these acids are brought together and that they no longer form a simple mixture, an explanation is afforded of their anomalous solubility. In support of this hypothesis, the following facts are adduced. (1) When a mixture of paranitrobenzoic acid with the ortho- or meta-acid is precipitated by hydrochloric acid from solution in caustic potash, its solubility is the same as that of a simple mixture of the acids in the same proportion; in the case, however, of a precipitated mixture of the ortho- and meta-acids, a considerable increase in solubility occurs. (2) Orthonitrobenzoic acid crystallises from its warm, aqueous solution in long needles, the appearance of which, under the microscope, is not changed when a considerable proportion of the para-acid is present; from a solution containing ortho- and meta-nitrobenzoic acid, however, ill-defined, arborescent crystals alone are obtained. That a change in the solid phase has here occurred is shown by the solubility in water of these crystals being different to that of the simple mixture of the acids. (3) The solubility in water of a finely pulverised mixture of paranitrobenzoic acid with either the ortho- or meta-acid is unchanged by being dissolved in ether and subsequently recovered by evaporating the solvent; when, however, a mixture of the ortho- and meta-acids is treated similarly, a considerable increase in solubility occurs.

W. A. D.

**Influence of Alkalis on Optically Active Acids.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, 17, 323—328).—When 10 grams of *d*-phenylglycollic acid is boiled for 17 hours with 100 c.c. of 10 per cent. aqueous potash, it is completely converted into the racemic modification; on boiling 7.6 grams of the same acid for 4 hours with 100 c.c. of normal caustic potash, only one-third, approximately, is racemised, whilst at the ordinary temperature practically no change can be detected in the rotatory power of the same solution after 66 days. Decinormal hydrochloric acid at its boiling point appears to be without action on *d*-phenylglycollic acid; at  $130$ — $135^{\circ}$ , however, partial decomposition into benzaldehyde and formic acid occurs.

Mucic acid, when heated with caustic alkalis of various concentrations, apparently undergoes decomposition without giving rise to allomucic acid, although the latter is formed, as Fischer has shown, when a solution of mucic acid is heated with pyridine; the recognition of allomucic acid is, however, rendered difficult by its salts, both metallic

and ethereal, being ill-defined and unsuitable for microchemical detection.

Saccharic acid (9.92 grams) is largely decomposed when boiled with 2*N* caustic potash (100 c.c.) for 24 hours; it is probable that manno-saccharic acid is first formed, which is subsequently further acted on by the alkali.

Neither camphoric acid (5 grams) nor quinic acid (9.6 grams) undergo change when boiled with 2*N* caustic potash (50 c.c.) for 24 hours. From this, and the preceding experiments, it appears that the transformation of optically active compounds into their inactive forms by caustic alkalis is far from being general; the difference in the behaviour of *d*-tartaric acid (Abstr., 1898, i, 515, and Boeseken, *ibid.*, 561) and the compounds dealt with above, awaits explanation.

W. A. D.

**Dyes from 5-Amidosalicylic Acid.** By ARMIN FISCHER and F. SCHAAR-ROSENBERG (*Ber.*, 1899, 32, 81—84).—5-Amidosalicylic acid is best prepared by the following process. A solution of 290 grams of sodium nitrite in 1 litre of water is added to a solution of 500 grams of aniline hydrochloride, 600 of hydrochloric acid (sp. gr. = 1.19), and 3000 of ice, and the diazotised solution run into a solution of 533 grams of salicylic acid and 2200 grams of crystallised sodium carbonate in 10 litres of water. The yellow sodium salt of the azo-acid is separated, washed with a little water, then made into a paste with water, and added to a warm solution of 1720 grams of stannous chloride in 3500 grams of hydrochloric acid (sp. gr. = 1.19); the clear solution is treated with its own volume of concentrated hydrochloric acid, and the precipitate, consisting of the hydrochlorides of aniline and of amidosalicylic acid, separated, washed with dilute hydrochloric acid (1 : 1), dissolved in 5 litres of water, and treated with its own volume of concentrated hydrochloric acid, when a 69 per cent. yield of the nearly pure amidosalicylic acid hydrochloride is obtained.

A rhodamine dye,  $C_{34}H_{22}N_2O_9$ , may be obtained as follows. A finely powdered mixture of amidosalicylic acid hydrochloride (75 grams) and of fluorescein chloride (75 grams) is heated in an oil-bath at 245° for 1 hour, and then at 280° for 2 hours, when it is completely molten. The powdered melt, which consists of the compound  $C_{34}H_{22}N_2O_9$  and a derivative of this obtained by the elimination of carbonic anhydride, is treated in an autoclave at 150° with an aqueous solution of 50 grams of sodium hydrogen carbonate, when the dye is obtained in solution in the form of its sodium salt. It is filtered warm, and the dye precipitated with hydrochloric acid; as all the sodium chloride cannot be removed by extraction with hot water, it is better to dry the crude product, extract the dye with alcohol, and then precipitate with water. When dried at 105°, it is a blue-violet powder, insoluble in cold and only sparingly soluble in hot water, insoluble in ether, benzene, ethylic acetate, or acetone, readily soluble in acetic acid or alcohol; its solutions in alkalis are violet, and exhibit a green fluorescence.

*α-Naphthaquinoneamidosalicylic acid*,  $C_{10}H_5O_2 \cdot NH \cdot C_6H_3(OH) \cdot COOH$ , obtained by the action of an alcoholic solution of amidosalicylic acid on *α*-naphthaquinone, crystallises from acetic acid in yellowish-red,

glistening needles, softens at 265°, and melts and decomposes at 278°, is insoluble in water or ether, sparingly soluble in alcohol or ethylic acetate; its solutions in ammonia or sodium carbonate are claret coloured, and in sodium hydroxide blue. J. J. S.

**Camphoric Acid.** V. By WILLIAM A. NOYES (*Amer. Chem. J.*, 1898, 20, 789—814).—The author gives the following correction of melting points quoted in an earlier paper (Abstr., 1896, i, 695), the ketone from *cis*-campholytic acid, 104° (not 112—113°); *aa*-dimethylketo-hexamethylene oxime, 115—117°, not 120—122° (compare Kipping, *Proc.*, 1896, 247, and Zelinski, *Ber.*, 1897, 30, 1543); and *α*-bromodihydro-*cis*-campholytic acid, 129—130° (instead of 124—125°).

It appears that 2-xylylidine is best obtained in small amounts from commercial xylylidine, of which it constitutes about 2 per cent.; 2-cyanometaxylylene, prepared from it by the Sandmeyer reaction, crystallises from light petroleum in white prisms, sublimes readily, melts at 89°, is easily soluble in alcohol and ether, and is hydrolysed only with very great difficulty.

Attempts to convert *aa*-dimethylketo-hexamethylene (Kipping, *Trans.*, 1895, 351) into hexahydro-1:6-dimethylbenzoic acid, by reducing it to the corresponding hexanol, replacing the hydroxyl by cyanogen, and hydrolysing the product, failed.

When bromine (1 mol.) is added to a solution of diethylic ethylidenedi-acetoacetate (Knoevenagel, *Abstr.*, 1895, i, 51), it is completely decolorised, no hydrogen bromide being evolved; on heating, during 10 minutes on the water-bath, the product which remains after evaporating the chloroform, and finally extracting with ether, a white powder is left undissolved consisting of 4-hydroxy-2:6-dimethylbenzoic acid; this dissolves with difficulty in water and chloroform, but more readily in alcohol, melts at 253—254°, and gives only a slight yellow coloration with ferric chloride. Hence it does not contain the hydroxyl group in the ortho-position relatively to the carboxyl, and can be considered as derived from the compound,  $\text{COOEt} \cdot \text{CH} \begin{smallmatrix} \text{CMe}=\text{CH} \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} \text{CO}$ ,

assumed by Knoevenagel (*loc. cit.*) to be present in the product obtained by heating diethylic ethylidenedi-acetoacetate with water at 140—150°. Its formation would then be analogous to that of symmetrical xylenol from 3:5-dimethyl- $\Delta^2$ -cyclohexenone under similar conditions (Knoevenagel, *loc. cit.*). The *ethylic* salt, which crystallises in plates or needles and melts at 98°, remains unchanged after long boiling with alcoholic potash, aqueous soda, or hydrobromic acid.

When the hydrazine compound, prepared from the bromoxylylidine obtained by Genz's method (*Ber.*, 1870, 3, 225) from 4-metaxylylidine, is treated with boiling aqueous copper sulphate according to Erdmann's directions (*Darst. org. chem. Präparate*, 71), it gives rise, not to the corresponding bromometaxylylene, but to 4-chloro-2-bromometaxylylene, which crystallises from alcohol in white leaflets, melts at 68°, and boils at 244°; it thus appears that Erdmann's directions for the elimination of an amido-group are seriously at fault. When, however, the amido-group is removed by other methods, a bromoxylylene is obtained which,

when boiled with acetic chloride and aluminium chloride in carbon bisulphide solution, is converted into an *acetyl bromometaxylylene*, which melts at  $33^{\circ}$  and boils at  $275\text{--}278^{\circ}$ . Since 5-bromometaxylylene yields an acetyl bromoxylylene which does not solidify in a freezing mixture, and since 4-bromometaxylylene does not give rise to an acetyl derivative under the above conditions, it follows, by exclusion, that in Genz's bromometaxylylene the bromine atom is in position 2. From Wróblewski's results, however (Abstr., 1878, 977), it would appear that the bromoxylylene has the symmetrical structure.

When 5-bromometaxylylene (5 grams), obtained from 5-bromo-xylydine by Sandmeyer's reaction, is boiled for three-quarters of an hour with aluminium chloride (5 grams) and acetic chloride (5 grams) in carbon bisulphide solution, it is converted into 4-*acetyl-5-bromometaxylylene*, which boils at  $272\text{--}276^{\circ}$ , and does not solidify in a freezing mixture. When oxidised by means of warm, alkaline potassium permanganate, this is converted into 5-*bromometaxylyl-4-glyoxylic acid*,  $\text{C}_6\text{H}_2\text{BrMe}_2\cdot\text{CO}\cdot\text{COOH}$ ; on adding dilute sulphuric acid to the hot solution without filtering off the manganese oxides, the glyoxylic acid is converted into 6-*bromo-2:4-dimethylbenzoic acid*, which crystallises from alcohol in long, slender needles and melts at  $183\text{--}184^{\circ}$ . Its structure follows from its yielding 2:4-dimethylbenzoic acid, when reduced with zinc dust and ammonia.

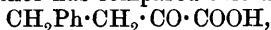
*Symmetrical iodoxylylene*, prepared from symmetrical xylydine, boils at  $117^{\circ}$  under a pressure of 27 mm., and at  $234\text{--}235^{\circ}$  under atmospheric pressure; when boiled (13.3 grams) with a mixture of carbon bisulphide (55 c.c.), aluminium chloride (11 grams) and acetic chloride (9 c.c.), for  $\frac{1}{2}$  hour on the water-bath, in a reflux apparatus, it is largely converted into 5-*iodo-4-acetylmetaxylylene*, which boils at  $171^{\circ}$  under a pressure of 25 mm., and at  $295\text{--}298^{\circ}$  with slight decomposition under atmospheric pressure. This, on oxidation with an ice-cold, alkaline solution of potassium permanganate, is converted into 5-*iodometaxylyl-4-glyoxylic acid*,  $\text{C}_6\text{H}_2\text{IME}_2\cdot\text{CO}\cdot\text{COOH}$ , which separates as an oil from the filtered solution on adding acid; the *barium* salt,  $(\text{C}_{10}\text{H}_8\text{IO}_3)_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ , is only sparingly soluble in hot water. When iodoxylylglyoxylic acid is oxidised by warming on the water-bath with an alkaline solution of potassium permanganate, and subsequently adding dilute sulphuric acid, it gives rise to 2(1-*iodo-4:6-dimethylbenzoic acid* and 2-*iodo-6-methylterephthalic acid*, which were separated by means of their barium salts. The first of these acids separates from alcohol in small, granular crystals, melts at  $196\text{--}197^{\circ}$ , and is converted by zinc dust and ammonia into 4:6-dimethylbenzoic acid; the *barium* salt is easily soluble in water, whilst the *copper* salt,  $(\text{C}_9\text{H}_8\text{IO}_2)_2\text{Cu} + n\text{H}_2\text{O}$ , is only slightly soluble. A second *iodo-4:6-dimethylbenzoic acid* was also isolated, which melted at  $172\text{--}173^{\circ}$  and differed from its congeners in being more easily soluble in water, the same being true of its copper salt; its *barium* salt,  $(\text{C}_9\text{H}_8\text{IO}_2)_2\text{Ba} + 6\text{H}_2\text{O}$ , however, crystallises from water in needles. The free acid, like its isomeride, is converted by reduction into 4:6-dimethylbenzoic acid. 2-*Iodo-6-methylterephthalic acid* crystallises from water in short, slender needles, and melts at  $298^{\circ}$ ; when treated with zinc dust and ammonia, it is converted into methylterephthalic acid, which melts

at 328—330°, not at 280—283° as stated by former observers (Fittig and Laubinger, *Annalen*, 151, 276; Remsen and Iles, *Amer. Chem. J.*, 1879, 1, 120). *Barium 2-iodo-6-methylterephthalate*,  $C_9H_5IO_4Ba + 6H_2O$ , rapidly effloresces, and is moderately soluble in water.

For preparing mesitylene, the author recommends a slightly modified form of Young and Orndorff's method (Abstr., 1893, i, 498), which gives much better results than those hitherto obtained. Acetylmesitylene, prepared by Meyer and Molz's method (*Ber.*, 1897, 30, 1271), boils at 240—241°, not at 235° as stated by Claus (Abstr., 1890, 981); when oxidised by an alkaline solution of potassium permanganate, it is converted into mesitylgyoxylic acid, which is transformed, on adding dilute sulphuric acid to the oxidising mixture, into trimethylbenzoic acid. On now adding the calculated quantity of alkaline potassium permanganate solution, subsequently warming, and finally adding sufficient sodium hydrogen sulphite to dissolve the precipitated manganese oxides, 2:6-dimethylterephthalic acid remains undissolved, whilst 3:5-dimethylphthalic acid passes into solution; the latter, when heated above its melting point, is converted into the anhydride,  $C_{10}H_8O_3$ , which crystallises from light petroleum in slender, white needles and melts at 116°. 4-Monomethyl 2:6-dimethylterephthalate crystallises from water or alcohol in needles, and melts at 189—190°; 2:6-dimethylterephthalamic acid,  $COOH \cdot C_6H_4Me_2 \cdot CO \cdot NH_2$ , prepared from it by the action of ammonia, crystallises from water in white needles, melts at 246°, and is converted by Hofmann's reaction into 4-amido-2:6-dimethylbenzoic acid, which crystallises from water in needles, and melts and decomposes at 194—195°. The hydrochloride is sparingly soluble in water; by evaporating its solution in hydrochloric acid to dryness on the water-bath, it is converted into 5-metaxylidine. 4-Iodo-2:6-dimethylbenzoic acid, prepared from the amido-acid, is easily reduced by zinc dust and 10 per cent. aqueous ammonia to 2:6-dimethylbenzoic acid, which crystallises from light petroleum in white needles and melts at 116°, not at 97—99° as stated by Jacobsen (*Ber.*, 1878, 11, 21).

W. A. D.

**Benzylpyruvic Acid.** By WILHELM WISLICENUS (*Ber.*, 1898, 31, 3133—3136).—The author has compared this acid,



as prepared by him by boiling ethylic benzyloxalacetate with 10 per cent. sulphuric acid for a day (Abstr., 1898, i, 299) with a sample obtained by Fittig by boiling phenylhydroxycrotonic acid with 5 per cent. caustic soda (*ibid.*, 196). The acid prepared by the first method is now found to give no coloration with ferric chloride when it has been purified by repeated boiling with dilute sulphuric acid. The acid does lose its water of crystallisation,  $1\frac{1}{2}H_2O$ , without any liquefying when placed over sulphuric acid in an exhausted desiccator in the dark; if exposed to light, it melts and volatilises slightly, but apparently undergoes no other change.

C. F. B.

**Action of Ethylic Chloroglyoxylate on Aromatic Hydrocarbons.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 940—943. Compare Abstr., 1897, i, 530, and 1898, i, 585).—*Ethyl paraxylglyoxylate* is obtained by treating purified paraxylene with



ethylic chloroglyoxylate and aluminium chloride in the usual manner; it is a colourless liquid and boils at 155—156° under a pressure of 10 mm.

Paraxylylglyoxylic acid, which melts sharply at 75° (compare Claus, Abstr., 1885, 1136), evolves carbonic oxide when heated with sulphuric acid at 100°, yielding paraxylylcarboxylic acid, and when heated with aniline gives rise to 2:5-dimethylbenzylideneaniline,  $C_6H_3Me_2 \cdot CH:NPh$ , which melts at 44°, boils at 177° (corr.) under a pressure of 10 mm. and dissolves readily in organic solvents. 2:5-Dimethylbenzaldehyde,  $C_9H_{10}O$ , is a colourless liquid having an odour of bitter almonds, and boils at 100° under 10 mm. pressure; the *hydrazone*,  $N_2(\cdot CH \cdot C_6H_3Me_2)_2$ , forms magnificent, yellow needles, melts at 124°, and is sparingly soluble in alcohol.

When a mixture of ethylic chloroglyoxylate and paracymene is treated with aluminium chloride, elimination of carbonic anhydride and carbonic oxide occurs and several products are formed. *Ethylcymene*,  $C_{12}H_{18}$ , is a colourless liquid having an odour of cymene, and boils at 97° under a pressure of 10 mm. and at 205° under atmospheric pressure. *Ethylic cymylglyoxylate*,  $C_{14}H_{18}O_3$ , boils at 180° under a pressure of 10 mm.; *cymylglyoxylic acid* was obtained as a liquid, and is probably a mixture of the two possible isomerides, as, on distillation, it yielded a mixture of aldehydes and a cymylcarboxylic acid which did not crystallise. *Cymophenone*,  $CO(C_{10}H_{13})_2$ , is a yellowish liquid which boils at 220° under a pressure of 10 mm.

When the foregoing cymylglyoxylic acid is heated with aniline, decomposition occurs, and the resulting phenylimide boils at 210° under a pressure of 10 mm.; the latter affords a mixture of aldehydes which boils at 120° under a pressure of 10 mm., and on treatment with hydrazine hydrate gives a small quantity of a crystalline hydrazone melting at 133°, the rest of the product being oily. When boiled with potash, the aldehydes yield a mixture of the corresponding alcohols and acids; the mixed alcohols boil at 128° under a pressure of 10 mm., whilst the acids, on fractional distillation, give a considerable quantity of a substance boiling at 170° which is identical with Claus' cymylcarboxylic acid [ $Me : Pr : COOH = 1 : 4 : 2$ ] and melts at 69°.

A. L.

**Glyoxylic Acids and Aldehydes Derived from Phenylic Ethers.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 943—947).—Ethylic chloroglyoxylate reacts energetically with anisole in presence of aluminium chloride, giving a liquid which boils at 183° under a pressure of 20 mm., and consists of a mixture of *ethylic para-* and *meta-methoxyphenylglyoxylates*,  $C_{11}H_{12}O_4$ , the former being present in predominating amount.

*Paramethoxyphenylglyoxylic acid*,  $OMe \cdot C_6H_4 \cdot CO \cdot COOEt$ , is easily obtained from the product of hydrolysis of the above mixture of ethereal salts; it forms beautiful needles, is sparingly soluble in boiling water, readily soluble in alcohol and ether, and less readily in benzene; when anhydrous, it melts at 93°; it yields anisic acid (m. p. = 184°) when distilled.

The presence of *metamethoxyglyoxylic acid* in the mother liquors was proved by treating the mixed acids with hydrazine sulphate and decomposing the hydrazone acids by means of heat; in this way, a mixture of the *hydrazones* of anisaldehyde and metamethoxybenzaldehyde was obtained. The former is nearly insoluble in alcohol and sparingly soluble in cold benzene, crystallises in beautiful, yellow leaflets, and melts at 166—167°, whereas the latter is more readily soluble and forms beautiful, yellow crystals melting at 141°.

*Ethylic 3 : 4-dimethoxyphenylglyoxylate*,  $C_6H_3(OMe)_2 \cdot CO \cdot COOEt$  [ $OMe : OMe : CO \cdot COOEt = 3 : 4 : 1$ ], is a somewhat viscous liquid boiling at 205° under a pressure of 10 mm.; the corresponding *amylic* salt boils at 220—225° under a pressure of 10 mm. *3 : 4-Dimethoxyphenylglyoxylic acid*,  $C_{10}H_{10}O_5$ , crystallises from benzene in small, white crystals and melts at 135—136°; it gives pure veratric acid when heated at its melting point. Veratric aldehyde was found to boil at 154—155° under a pressure of 10 mm.; the *hydrazone*,  $N_2(C_9H_{10}O_2)_2$ , is insoluble in water and the ordinary neutral solvents, and forms yellow crystals melting at 190°; the *phenylimide* is a very viscous, yellow oil, and boils at 235° under 10 mm. pressure.

*2 : 4-Dimethoxyphenylglyoxylic (dimethylresorcinolglyoxylic) acid*,  $C_6H_3(OMe)_2 \cdot CO \cdot COOEt$ , obtained by the decomposition of the corresponding ethylic salt, crystallises from alcohol or water in small crystals which contain  $1H_2O$  and melt at 65—70°; the anhydrous acid melts at 108°. By the action of aniline, it yields *2 : 4-dimethoxybenzylideneaniline*,  $C_6H_3(OMe)_2 \cdot CH : NPh$ , which is a thick, yellow oil boiling at 245° under a pressure of 10 mm.; it is readily decomposed with formation of *2 : 4-dimethoxybenzaldehyde* (dimethylresorcylic aldehyde),  $C_6H_3(OMe)_2 \cdot COH$ , which boils at 165° under a pressure of 10 mm. and melts at 68°.

*Ethylic 3 : 6-dimethoxyphenylglyoxylate* (dimethylhydroquinoneglyoxylate) was not isolated, but was transformed into the phenylimide of *3 : 6-dimethoxybenzaldehyde*; the aldehyde itself melts at 51° and boils at 146° under 10 mm. pressure.

A. L.

**Phenolglyoxylic Acids.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 947—949).—Simple phenols and their acidyl compounds do not react with ethylic chloroglyoxylate under the conditions employed by the author in other cases. Phenylic picrate, however, reacts with ethylic chloroglyoxylate in presence of aluminium chloride, and yields some quantity of the *picrate* of *ethylic parahydroxyphenylglyoxylate*,  $C_6H_2(NO_2)_3 \cdot O \cdot C_6H_4 \cdot CO \cdot COOEt$ ; this is easily hydrolysed by means of potash, yielding *potassium parahydroxyphenylglyoxylate* and picrate. Free parahydroxyphenylglyoxylic acid is decomposed by heat into parahydroxybenzoic acid and the corresponding aldehyde; a better yield of the latter is obtained by using hot dimethylaniline.

When picrylguaiacol is treated in the above manner, an *acid* is produced which is very soluble in hot water, less readily in cold water, and which probably has the constitution  $OMe \cdot C_6H_3(OH) \cdot CO \cdot COOH$  [ $OH : OMe : CO \cdot COOEt = 3 : 4 : 1$ ].

A. L.

**Three Cases of Desmotropism.** By PAUL RABE (*Ber.*, 1899, 32, 84—90. Compare Knorr, *Abstr.*, 1897, i, 63; Schiff, *Abstr.*, 1898, i, 237, 355, 424, 464).—The author thinks that no definite conclusions can be drawn as to the composition of a mixture of desmotropic substances by conversion into derivatives by the aid of chemical reagents, and has, therefore, restricted himself to the isolation of solid desmotropic forms. The enolic forms of ethylic alkylidenebisacetoacetates are readily isolated by adding the sodium salts to an excess of well cooled dilute sulphuric acid and extracting with ether.

The ethylic benzylidenediacetoacetate melting at 152° (compare Schiff, *loc. cit.*) is the ketonic form; it dissolves slowly in sodium hydroxide and is insoluble in sodium carbonate. When treated with sodium ethoxide, it yields the sodium derivative, from which the enolic form can be isolated; this melts at about 60°, but becomes transformed into the ketonic form; it differs from the ketonic form in the deep red-violet coloration which its alcoholic solution gives with ferric chloride and in its ready solubility in ether.

The ketonic form of ethylic ethylidenediacetoacetate melts at 80°, gives no coloration in alcoholic solution with ferric chloride, and on fusion or solution readily passes into the enolic form; the latter crystallises from alcohol in rhombic plates, and melts at 60—61°, but at the same time becomes converted into the ketonic form.

The compound obtained by Goldschmidt and Kisser (*Abstr.*, 1887, 475) from ethylic acetoacetate and carvone probably has the ketonic constitution, as it is insoluble in sodium carbonate and gives no coloration with ferric chloride. The *enolic* form has been obtained as an oily liquid which so far has not been reconverted into the ketonic form.

J. J. S.

**Condensation of "Saccharin" with Phenols.** By PAUL SISLEY (*Bull. Soc. Chim.*, 1897, [iii], 17, 821—823).—It is pointed out that compounds analogous to, if not identical with, the substances obtained by Monnet and Ketschet by the condensation of "saccharin" with phenols (this vol., i, 212), have been previously prepared and described by the author, in conjunction with Seyewetz, in their work "*La chimie des matières colorantes artificielles.*" When treated with concentrated mineral acids, the "sacchareins" of Monnet and Ketschet lose ammonia, and yield substances identical with the "sulphureins" obtained by Remsen and by the author. Details are given of the preparation and properties of resorcinolsulphurein and tetrabromoresorcinolsulphurein.

N. L.

**The Sacchareins. A Reply to Sisley.** By PAUL MONNET and J. KETSCHET (*Bull. Soc. Chim.*, 1897, [iii], 17, 1030—1031).—The authors claim priority over Seyewetz and Sisley in the preparation of colouring matters by the condensation of saccharin with resorcinol (compare this vol., i, 212), and state that the compounds prepared by the latter are derived from sulphobenzoic acid and not from "saccharin."

T. M. L.

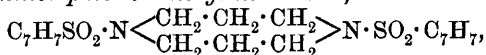
**Preparation of Secondary Amines from Sulphonamides.** By WILHELM MARCKWALD and ALBERT (FREIHERR) VON DROSTE-HUELSHOFF (*Ber.*, 1898, 31, 3261—3266).—Secondary amines can be

prepared from unsubstituted sulphonamides by a reaction similar to that employed by Hinsberg (Abstr., 1892, 64) for their preparation from monosubstituted sulphonamides.

Benzenesulphonamide is converted by ethylenic bromide and soda, first into dibenzenesulphoethylenediamide (Abstr., 1896, i, 47), and then into *dibenzenesulphopiperazide*,  $\text{SO}_2\text{Ph}\cdot\text{N}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{N}\cdot\text{SO}_2\text{Ph}$ , which is very sparingly soluble in all solvents, and forms microscopic crystals melting at  $282-283^\circ$  (German Patents 70055 and 70056). When a monohalogen alkyl is employed, disubstituted sulphonamides are readily produced; thus paratoluenesulphonamide is converted into *paratoluenesulphodiethylamide*, which crystallises well and melts at  $60^\circ$ . The disubstituted amine is best obtained by heating the sulphonamide with chlorosulphonic acid, since in this way the original sulphochloride is regenerated and a disubstituted amidosulphonic acid produced which is readily decomposed by alkalis,  $\text{R}\cdot\text{SO}_2\cdot\text{NR}'_2 + \text{Cl}\cdot\text{SO}_3\text{H} = \text{R}\cdot\text{SO}_2\text{Cl} + \text{SO}_3\text{H}\cdot\text{NR}'_2$ ; paratoluenesulphodiethylamide, when treated in this way, yields paratoluenesulphochloride and diethylamine.

Two distinct compounds are produced by the action of trimethylenic bromide on paratoluenesulphonamide in the presence of alkali. *Paratoluenesulphotrimethyleneimide*,  $\text{C}_7\text{H}_7\text{SO}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}_2$ , crystallises in long needles melting at  $120^\circ$ . The trimethyleneimine ring is decomposed by acids, but can be removed from the sulphonic compound by nascent hydrogen; these reactions are still under investigation.

*Diparatoluenesulphobis(trimethylenedi-imide)*,

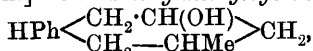


crystallises in large, silvery plates, and melts at  $215^\circ$ .

A. H.

**Hydrogenised Aromatic Compounds.** By EMIL KNOEVENAGEL (*Annalen*, 1898, 303, 259—274. Compare Abstr., 1897, i, 606).—The author has already shown that hydrogenised derivatives of toluene, metaxylene, &c., may be prepared from the 1:5-diketones which arise from condensation of ethylic acetoacetate with aldehydes of the acetic series. It is now found that if aromatic aldehydes are substituted for the compounds last named, hydrogenised derivatives of the diphenyl series are obtained.

[With J. GOLDSMITH.]—3:1-*Phenylmethylcyclohexanol-5*,



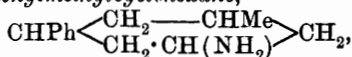
obtained by reducing phenylmethylcyclohexenone (Abstr., 1895, i, 50) in absolute alcohol with sodium, is a viscous, colourless liquid which boils at  $155-159^\circ$ ,  $166-169^\circ$ , and  $176-178^\circ$  under pressures of 6 mm., 10 mm., and 20 mm. respectively; it has the sp. gr. = 1.024 at  $18^\circ/4^\circ$ , and the refractive index  $n_D = 1.5395$  at  $18^\circ$ . The ether,  $\text{C}_{26}\text{H}_{34}\text{O}$ , which melts at  $80-100^\circ$ , and boils above  $300^\circ$  under a pressure of 10 mm., remains in the form of a red, transparent resin when the alcohol is distilled; it has a green reflex, and is yellow when powdered. The *acetyl* derivative is a limpid oil

which boils at 173—174° and 294—297° under pressures of 10 mm. and 760 mm. respectively; it has the sp. gr. = 1·0254 at 20°/4°, and the refractive index  $n_D = 1·5155$  at 20°.

3 : 1-Phenylmethylcyclohexene,  $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \text{---CH} \end{smallmatrix} \text{CH}_2$ , or  $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}=\text{CH} \end{smallmatrix} \text{CH}_2$ , prepared by heating phenylmethylcyclohexanol with phosphoric anhydride, is a limpid oil which boils at 128—130°, 146—150°, and 248—252° under pressures of 17 mm., 32 mm., and 760 mm. respectively; it has a sp. gr. = 0·9581 at 22°/4°, and the refractive index  $n_D = 1·5402$  at 22°.

3 : 1-Phenylmethylcyclohexanone-5,  $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 \text{---CO} \end{smallmatrix} \text{CH}_2$ , prepared by oxidising the corresponding alcohol with chromic acid, is a colourless oil which boils at 168—170° under a pressure of 16 mm.; the *oxime* separates from petroleum as a white, crystalline powder which melts at 105° (compare this vol., i, 25).

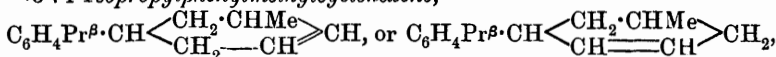
5-Amido-3 : 1-phenylmethylcyclohexane,



prepared by reducing the foregoing oxime with sodium in absolute alcohol, has a feeble odour of piperidine, and boils at 180—185° under a pressure of 40 mm.; the *hydrochloride* crystallises from water in lustrous leaflets and melts at 205—207°.

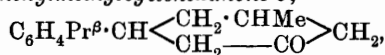
[With K. WEDEMEYER and F. GIESE]—3 : 1-Isopropylphenylmethylcyclohexanol-5,  $\text{C}_6\text{H}_4\text{Pr}^\beta \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{CH}_2 \text{---CHMe} \end{smallmatrix} \text{CH}_2$ , prepared by reducing isopropylphenylmethylcyclohexenone with sodium and absolute alcohol, boils at 185° under a pressure of 14 mm.; the *acetyl* derivative is a colourless, viscous liquid which boils at 206° under a pressure of 14 mm., and has a disagreeable odour. Treatment with glacial acetic acid saturated with hydrogen iodide converts the alcohol into a *compound* which is either the cyclohexene,  $\text{C}_{16}\text{H}_{22}$ , or the cyclohexane,  $\text{C}_{16}\text{H}_{24}$ ; it boils at 153—157° under a pressure of 10 mm.

3 : 1-Isopropylphenylmethylcyclohexene,



arises from the foregoing alcohol under the influence of phosphoric anhydride, and boils at 149—150° under a pressure of 12 mm.; it has a sp. gr. = 0·9376 at 14°/4°, and the refractive index  $n_D = 1·5283$  at 14°.

3 : 1-Isopropylphenylmethylcyclohexanone-5,



melts at 67·5° and boils at 187° under a pressure of 11 mm.; the *semicarbazone* melts at 142°.

M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Diphenyl in the Presence of Aluminium Chloride. By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 809—811).—When ethylic chloroglyoxylate is added to a solution of diphenyl in boiling

carbon bisulphide containing aluminium chloride, the theoretical amount of hydrogen chloride is evolved, and *ethylic diphenylglyoxylate*,  $C_6H_4Ph \cdot CO \cdot COOEt$ , is formed; this distils at about  $232^\circ$  under a pressure of 9 mm., and crystallises from light petroleum in colourless plates melting at  $39^\circ$ . On hydrolysis, it yields *diphenylglyoxylic acid*, a colourless, crystalline substance melting at about  $170^\circ$ , and very soluble in the ordinary solvents. On boiling with aniline, this acid yields a *phenylimide*, which is decomposed by dilute sulphuric acid with formation of *phenylbenzaldehyde*; this crystallises in groups of small, colourless needles, melts at  $57^\circ$ , boils at  $184^\circ$  under a pressure of 11 mm., and is very soluble in ordinary solvents, with the exception of light petroleum. The *hydrazone*,  $N_2(:CH \cdot CHPh)_2$ , crystallises from benzene in brilliant, yellow plates melting at about  $245^\circ$ . The constitution of the compounds described above is established by the fact that phenylbenzaldehyde is oxidised to paraphenylbenzoic acid by potassium permanganate in alkaline solution.

Attempts were made to introduce a 'glyoxylic residue into each of the phenyl groups in diphenyl, in order to obtain a dialdehyde, but without success. N. L.

**Compounds from Benzoic or Phthalic Chloride and Ethereal Salts of the Three Hydroxybenzoic Acids.** By HEINRICH LIMPRICHT (*Annalen*, 1898, 303, 274—289. Compare Abstr., 1896, i, 435).—When benzoic or phthalic chloride acts on an ethereal salt of orthohydroxybenzoic acid, the chlorine combines with hydrogen from the benzene ring, yielding benzoylsalicylic acid,  $COPh \cdot C_6H_3(OH) \cdot COOH$ , and disalicylphthalide,  $CO \langle \underset{O}{C_6H_4} \rangle C[C_6H_3(OH) \cdot COOH]_2$ . In the case of the meta- and para-hydroxybenzoic acids, however, it is the hydrogen of the phenolic group which suffers attack, giving rise to ethylic benzoyloxybenzoates,  $COOEt \cdot C_6H_4 \cdot O \cdot COPh$ , and ethylic phthalylloxybenzoates,  $CO \langle \underset{O}{C_6H_4} \rangle C(O \cdot C_6H_4 \cdot COOEt)_2$ . The general method of preparing these substances consists in heating benzoic or phthalic chloride in carbon bisulphide with aluminium chloride.

*Ethylic metaphthalylloxybenzoate* forms colourless, wedge-shaped, triclinic crystals, and melts at  $66^\circ$ ; alkalis and hydrochloric acid resolve it into metahydroxybenzoic and phthalic acids.

*Ethylic parabenzoyloxybenzoate* separates from ether in colourless, monoclinic crystals and melts at  $89^\circ$ . *Ethylic paraphthalylloxybenzoate* forms rhombic crystals and melts at  $97^\circ$ .

*Ethylic metabenzamidobenzoate*,  $COPh \cdot NH \cdot C_6H_4 \cdot COOEt$ , melts at  $114^\circ$ ; hydrolysis resolves it into benzoic and amidobenzoic acids.

*Ethylic metaphthalamidobenzoate*,  $CO \langle \underset{O}{C_6H_4} \rangle C(NH \cdot C_6H_4 \cdot COOEt)_2$ , melts at  $191^\circ$ .

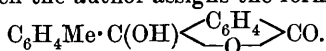
*Ethylic paramidobenzoate*,  $NH_2 \cdot C_6H_4 \cdot COOEt$ , separates from ether in rosettes of rhombic crystals and melts at  $89^\circ$ ; the *benzoyl* derivative crystallises from alcohol in white leaflets and melts at  $148^\circ$ . *Ethylic paraphthalamidobenzoate* separates from ethylic acetate in highly lustrous, monoclinic crystals and melts at  $188^\circ$ ; the *com-*

pound,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{COOEt}$ , is produced when phthalic chloride acts on ethylic paramidobenzoate in molecular proportion.

*Phthalylsalicylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4(\text{OH}) \cdot \text{COOH}$ , results from the action of phthalic chloride on salicylic acid in carbon bisulphide under the influence of aluminium chloride; it separates from alcohol in monosymmetric crystals, and melts at  $244^\circ$ . The *barium* and *silver* salts are anhydrous, the former being red. *Disalicylphthalide*, which is obtained in the form of its methylic salt in association with phthalylsalicylic acid, crystallises from alcohol in slender, colourless needles and melts at  $276^\circ$ ; hydrochloric acid at  $190^\circ$  resolves it into phenol, phthalic acid, and carbonic anhydride. The *barium* salt is a deep red, microscopic powder, and the *silver* salt rapidly becomes black; the *methylic* salt crystallises from alcohol in leaflets and melts at  $171^\circ$ . The *ethylic* salt melts at  $144^\circ$ .

*Disalicylorthotoluic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}[\text{C}_6\text{H}_4(\text{OH}) \cdot \text{COOH}]_2$ , prepared by reducing disalicylphthalide with zinc dust and ammonia, is precipitated by toluene from the ethereal solution as an amorphous powder; it softens at  $145^\circ$ , evolves gas, and then solidifies at about  $152^\circ$ , and subsequently fuses at  $251^\circ$ . The *barium* salt is a white, microcrystalline powder. M. O. F.

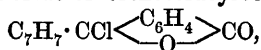
Syntheses by means of Phthalyl Tetrachloride (m. p.  $88^\circ$ ).  
 II. Homologues of Diphenylanthrone. [I.] By ALFRED GUYOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 966—982. Compare this vol., i, 221). —The author shows that, when ditolylphthalide is prepared by condensing phthalyl chloride with toluene, a small quantity of ditolylanthrone is also produced, on account of the presence of phthalyl tetrachloride in the commercial dichloride. The purification of the ditolylphthalide can be readily effected by dissolving it in alcoholic potash, diluting with water, and boiling the filtered solution, when the unstable potassium salt is decomposed and the phthalide reproduced; this formation of a lactone on boiling the aqueous solution is characteristic of the salts of all derivatives of phenylcarbinolorthocarboxylic acid. A better yield of ditolylphthalide is obtained by the action of aluminium chloride on the chloride of the so-called paratoluoylorthobenzoic acid, to which the author assigns the formula



By the action of zinc dust on an alkaline solution of ditolylphthalide, *ditolylphenylmethaneorthocarboxylic acid*,  $\text{CH}(\text{C}_7\text{H}_7)_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , is produced, and a smaller yield of the same substance can be obtained by the condensation of tolylphthalide with toluene; it melts at  $172^\circ$ , dissolves readily in most organic solvents, and separates from alcohol in colourless crystals; the alkali salts are very soluble in water, alcohol, and ether, and do not crystallise on evaporating the solution; the *barium* salt,  $\frac{2}{3}(\text{C}_{22}\text{H}_{19}\text{O}_2)_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$ , forms long needles. By the action of phosphorus pentachloride or of sulphuric acid, it is converted into *tolyl-3-methylantranol*,  $\text{C}_6\text{H}_4 \langle \text{C}(\text{C}_7\text{H}_7) \rangle \text{C}(\text{OH}) \text{C}_6\text{H}_3\text{Me}$ ; this was not analysed, but by dissolving it in acetic acid and adding potassium

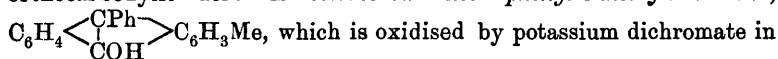
dichromate it was converted directly into *tolyl-3-methyloxanthranol*,  $C_6H_4 \begin{smallmatrix} \text{C(OH)C}_7H_7 \\ \text{CO} \end{smallmatrix} > C_6H_3Me$ ; the latter substance separates from toluene in slender, colourless needles, and melts at  $206^\circ$ ; it can be prepared directly from ditolylphthalide and phosphorus pentachloride by the author's method (*loc. cit.*), but the yield is poor.

Phenyltolylphthalide is best prepared by the condensation of toluene with the chloride of orthobenzoylbenzoic acid,  $CPhCl \begin{smallmatrix} \text{C}_6H_4 \\ \text{O} \end{smallmatrix} > CO$ , or of benzene with the chloride of orthotoluoylbenzoic acid,



in presence of aluminium chloride. When dissolved in alcoholic potash, it is reduced by zinc dust to *diphenyltolylmethaneorthocarboxylic acid* (*phenyltolylorthotoluic acid*),  $C_7H_7 \cdot CHPh \cdot C_6H_4 \cdot COOH$ ; this, which is isomeric with the acid,  $CHPh_2 \cdot C_6H_4 \cdot Me \cdot COOH$ , prepared by Hémilian (Abstr., 1887, 266), is also produced in smaller yield by the direct condensation of toluene with monophenylphthalide in presence of aluminium chloride; it melts at  $172^\circ$ , and when distilled with anhydrous baryta under reduced pressure is converted into paratolyl-diphenylmethane. The acid obtained by Gresly (Abstr., 1886, 1035) by the action of aluminium chloride on a solution of tolylphthalide in benzene, is not identical with that just described; the author shows that it is converted into triphenylmethane by distillation with anhydrous baryta, and that its melting point agrees with that of triphenylmethaneorthocarboxylic acid; its formation indicates that under the influence of the aluminium chloride the methyl group of the tolylphthalide must have been transferred to the excess of benzene used as a solvent, just as toluene is itself converted by the action of aluminium chloride into a mixture of benzene and xylene.

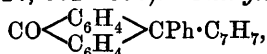
By the action of concentrated sulphuric acid, diphenyltolylmethaneorthocarboxylic acid is converted into *phenyl-3-methylantranol*,



acetic acid solution into phenyl-3-methyloxanthranol; the latter can also be prepared directly from phenyltolylphthalide and phosphorus pentachloride by the author's method, but the yield is small; it melts at  $216^\circ$ , and dissolves readily in ether, benzene, toluene, and acetic acid; its constitution is established by its conversion into tolylphenyl-3-methylantrone, and also by its preparation from Hémilian's diphenylparatolylmethaneorthocarboxylic acid [ $CH_3 : COOH : CHPh_2 = 1 : 3 : 4$ ].

T. M. L.

**Synthesis by Means of Phthalyl Tetrachloride (m. p.  $88^\circ$ ).**  
**II. Homologues of Diphenylantrone.** [II.] By H. GUYOT (*Bull. Soc. Chim.*, 1897, [iii], 17, 982—990).—*Phenyltolylantrone*,



prepared by the condensation of phenyloxanthranol or its chloride with toluene, melts at  $209^\circ$  (corr.), and can be sublimed and distilled without decomposition; it dissolves readily in cold benzene, toluene,



acetic acid, chloroform, and nitrobenzene, but is only sparingly soluble in alcohol, ether, or light petroleum; the molecular weight is normal.

*Phenyltolyl-3-methylanthrone*,  $\text{CO} \langle \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_3\text{Me} \rangle \text{CPh} \cdot \text{C}_7\text{H}_7$ , prepared by the condensation of phenyloxanthranol with benzene by means of concentrated sulphuric acid, melts at  $176^\circ$ , sublimes without decomposition, and shows a normal molecular weight. The isomeric *ditolylanthrone*,  $\text{CO} \langle \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \rangle \text{C}(\text{C}_7\text{H}_7)_2$ , prepared by the action of aluminium chloride on a solution of dichloranthrone (anthraquinone dichloride) in toluene, separates from nitrobenzene in large, transparent, monosymmetric prisms, of which measurements are given, and melts at  $235^\circ$ ; it is almost insoluble in alcohol and ether, but dissolves readily in nitrobenzene, benzene, toluene, and chloroform, and shows a normal molecular weight. These two substances are isomeric with Hallgarten's dibenzylanthrone.

*Ditolyl-3-methylanthrone*,  $\text{CO} \langle \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4\text{Me} \rangle \text{C}(\text{C}_7\text{H}_7)_2$ , is obtained as an impurity in the preparation of ditolylphthalide from phthalyl dichloride and toluene, but is also formed by the condensation of toluene with tolyl-3-methyloxanthranol by means of sulphuric acid. The best method of preparation is, however, by the action of aluminium chloride on a mixture of phthalyl tetrachloride and toluene, in which case dichloro-3-methylanthrone and tolylchloro-3-methylanthrone are formed as intermediate products. It also appears as a bye-product when paratoluylorthobenzoic acid is treated with an excess of phosphorus pentachloride, and subsequently with toluene and aluminium chloride for the preparation of ditolylphthalide; its formation indicates that the toluoylbenzoic acid is partially converted into dichloro-3-methylanthrone,  $\text{C}_6\text{H}_4 \langle \text{CCl}_2 \text{---} \text{CO} \rangle \text{C}_6\text{H}_3\text{Me}$ , just as ditolylphthalide is converted by phosphorus pentachloride into tolylchloro-3-methylanthrone,  $\text{CO} \langle \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_2\text{Me} \rangle \text{CCl} \cdot \text{C}_7\text{H}_7$ . The substance is almost insoluble in alcohol, ether, and light petroleum, but dissolves readily in chloroform, benzene, toluene, and nitrobenzene; it melts at  $217^\circ$ , and shows a normal molecular weight.

The author points out that, in all the cases described, condensation takes place more readily with toluene than with benzene.

T. M. L.

**Two New Hydrocarbons.** By PAUL COHN (*Chem. Centr.*, 1898, ii, 284; from *Österr. Chem. Zeit.*, 1, 137—138).—According to the author, a hydrocarbon,  $\text{C}_{21}\text{H}_{20}$ , which is probably symmetrical *triphenylpropane*, is obtained as a viscous oil of pleasant odour when 10 grams of cyclophenylenebenzylidene oxide or 10 grams of ortho-hydroxybenzhydramine is heated at  $140\text{--}150^\circ$  with 40—50 c.c. of fuming hydriodic acid and 5 grams of red phosphorus. The liquid, after shaking with ether, is made alkaline, distilled with steam, shaken with ether, and the ethereal extract evaporated. From the fractions distilling at  $200\text{--}360^\circ$ , of the other heavy hydrocarbons

which are formed, the author has isolated a hydrocarbon,  $C_{28}H_{26}$ , which is probably symmetrical *tetraphenylbutane*. E. W. W.

**Application of Schiff's Reaction to some Substituted Magentas.** By PAUL CAZENEUVE (*Bull. Soc. Chim.*, [iii], 17, 998—999).—The author has shown (Abstr., 1898, i, 568) that magenta S does not give Schiff's reaction on reducing it with sulphurous acid and then adding aldehyde; he now shows that, whilst the homologues of magenta are very sensitive, their sulphonic acid derivatives resemble magenta S in giving no coloration when treated in this way.

T. M. L.

**Transformation of Orthotolylic Carbonate into a Phthalein Derivative.** By PAUL CAZENEUVE (*Compt. rend.*, 1898, 127, 1021—1023).—Orthotolylic carbonate undergoes oxidation when mixed with soda lime in the presence of atmospheric oxygen, and an aqueous extract of the product, on treatment with acid, yields an insoluble, maroon-coloured, uncrystallisable compound whose composition corresponds with the formula  $C_{23}H_{20}O_4$ . The new substance behaves like a phthalein, but has no affinity for animal and vegetable fibres; it dissolves in ammonia and dilute alkalis. Its *acetyl* derivative is also uncrystallisable and insoluble in dilute alkalis; in concentrated alkaline solutions, it undergoes hydrolysis, yielding the original phthalein. Guaiacol carbonate, treated in a similar manner, yields a very slight amount of colouring matter, whilst under these conditions meta- and para-tolylic carbonates undergo no change.

G. T. M.

**Application of Perkin's Reaction to some Aldehydes of the Naphthalene Series.** By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 812—816).—*a*-Naphthaldehyde, when heated at  $180^\circ$  with acetic anhydride (3 parts) and sodium acetate (1 part), yields only *a*-naphthylacrylic acid, a crystalline substance melting at  $205^\circ$ , which has been previously prepared by Lugli. On distillation at the ordinary pressure, this acid passes over unchanged, instead of yielding *a*-naphthylethylene, as was expected. When heated with propionic anhydride and sodium propionate, *a*-naphthaldehyde yields chiefly neutral products, among which is *a*-naphthylpropylene, a liquid boiling at  $137$ — $138^\circ$  under 10 mm. pressure and forming a *picrate*,  $C_{10}H_7 \cdot CH : CHMe, C_6H_3N_3O_7$ , which crystallises in red needles melting at  $110^\circ$ . There is also formed, however, a small quantity of *a*-naphthylpropylenecarboxylic acid,  $C_{10}H_7 \cdot CH : CMe \cdot COOH$ , which crystallises from benzene in slender, white needles melting at  $151^\circ$ , and is probably the first product of the reaction.

1:4-Methoxynaphthaldehyde reacts with acetic anhydride and sodium acetate to form 1:4-methoxynaphthylacrylic acid, a crystalline solid melting at  $214^\circ$ . With propionic anhydride and sodium propionate, it yields only neutral products, among which is a liquid of the formula  $OMe \cdot C_{10}H_6 \cdot CH : CHMe$ , which boils at  $170$ — $171^\circ$  under a pressure of 9 mm., and has an odour of cloves. This substance, which may be regarded as the anethoil corresponding with naphthalene, forms a *picrate* crystallising in dark, reddish-brown needles

melting at  $120^{\circ}$ , and combines with 2 atoms of bromine to form a viscous additive product which could not be crystallised.

1:4-Ethoxynaphthaldehyde, when treated with propionic anhydride and sodium propionate, yields 1:4-ethoxynaphthylpropylene,  $\text{OEt} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH}:\text{CHMe}$ , a liquid boiling at  $177\text{--}178^{\circ}$  under a pressure of 9 mm., and forming a *picrate* which crystallises in slender, reddish-brown needles melting at  $137\text{--}138^{\circ}$ .

$\beta$ -Naphthaldehyde, when heated for 3 days with acetic anhydride and sodium acetate, yields a small quantity of  $\beta$ -naphthylacrylic acid, which crystallises in small grains melting at  $196^{\circ}$ . 1:2-Methoxynaphthaldehyde, when similarly treated, yields neither an acid nor any derivative thereof.

It appears, from these results, that Perkin's reaction is readily applicable to  $\alpha$ -naphthaldehyde and to 1:4-alkyloxynaphthaldehydes, whilst it is only effected with difficulty in the case of  $\beta$ -naphthaldehyde, and fails altogether with 1:2-alkyloxynaphthaldehydes.

N. L.

**Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on  $\alpha$ -Ethoxynaphthalene in the Presence of Aluminium Chloride.** By L. ROUSSET (*Bull. Soc. Chim.*, 1897, [iii], 17, 811—812. Compare Abstr., 1898, i, 591).—Ethylic chloroglyoxylate reacts with  $\alpha$ -ethoxynaphthalene in the presence of aluminium chloride to form ethylic  $\alpha$ -ethoxynaphthylglyoxylate, which crystallises from alcohol in brilliant, white plates melting at  $83^{\circ}$ , and boiling at  $240\text{--}245^{\circ}$  under a pressure of 10 mm. On hydrolysis, it yields  $\alpha$ -ethoxynaphthylglyoxylic acid, melting at  $160^{\circ}$ ; and, when treated with aniline, forms a *phenylimide*, which crystallises from benzene in small, yellow grains melting at  $72^{\circ}$ . When this phenylimide is boiled with dilute sulphuric acid, it is converted into  $\alpha$ -ethoxynaphthaldehyde, a crystalline solid melting at  $72^{\circ}$ . This forms a *hydrazone* which crystallises from xylene in small, yellow grains melting at  $204^{\circ}$ , and very slightly soluble in ordinary solvents. The analogy of the compounds just described with those obtained from  $\alpha$ -methoxynaphthalene, justifies the assumption that in  $\alpha$ -ethoxynaphthalene the entering radicle takes up the para-position with regard to the ethoxyl group. Thus,  $\alpha$ -ethoxynaphthaldehyde has the constitution  $\text{C}_{10}\text{H}_6(\text{OEt}) \cdot \text{COH}$  [ $\text{OEt} : \text{COH} = 1:4$ ].

N. L.

**Cryoscopic Researches in the Terpene Series.** By WILHELM BILTZ (*Zeit. physikal. Chem.*, 1898, 27, 529—551).—The molecular depressions of the freezing point were determined for solutions of a large number of compounds of the terpene series, benzene being employed as a solvent and observations being in all cases made at various concentrations. Curves representing molecular weight against depression are given, and it is seen that for all those compounds which are known to contain no hydroxyl, the curves are almost parallel to the horizontal axis, that is, the molecular weight found is almost constant, increasing but slightly with concentration. Curves of this type are given by fenchone, menthone, tanacetone, isothujone, pulegone, carvone, dihydrocarvone, citronellaldehyde, citral, cineol, and pinol. Carvenone gives a similar normal curve, and hence is most

probably ketonic, although certain of its physical properties indicate an alcoholic constitution (Abstr., 1895, i, 672). Hydroxylic compounds give curves, which rise rapidly with increase of concentration, and lead to abnormally high molecular weights (Auwers, Abstr., 1893, ii, 133; 1895, ii, 42). The curves for citronellylic alcohol and geraniol ascend rapidly, but are not quite so steep as that given by ethylic alcohol; these may be regarded as types of curves for primary alcohols. For menthol, dihydrocarveol, and *l*-borneol, which contain secondary hydroxyl, the ascent is less steep, whilst for the tertiary alcohols linalool, terpineol, *cis*-terpin (in naphthalene solution), the ascent, although evident, is still less marked. Borneol and isoborneol give different curves, that of the former being typical of a secondary alcohol, whilst that of the latter resembles those of the tertiary alcohols, although such constitution is not in accord with its chemical behaviour.

L. M. J.

**Additive Compounds of Formaldehyde with Terpenes.** By O. KRIEWITZ (*Ber.*, 1899, 32, 57—60).—Pinene boiling at 156—159° (20 grams), paraformaldehyde (4.4 grams), and alcohol (10 grams) are heated in sealed tubes at 170—175° for 12 hours, the contents then poured into water, and extracted with ether; a considerable quantity of terpene is recovered, and an oil boiling at 225—240° is collected separately. After purification by distillation with steam, and several fractionations, this distils at 232—236°, and has the composition  $C_{11}H_{18}O$ ; it is a clear, somewhat viscid, strongly dextrorotatory liquid of sp. gr. = 0.961 at 20°, with an odour like that of turpentine, and is readily soluble in most organic solvents, but insoluble in water. The yield is only some 15 per cent. of the theoretical. It forms a *dihydrochloride*,  $C_{13}H_{18}OCl_2$ , which crystallises from light petroleum in glistening plates, melts at 74°, is optically inactive, and readily soluble in alcohol, ether, or benzene. The corresponding *dihydrobromide* melts at 77°, and the *acetyl* derivative,  $C_{13}H_{20}O_2$ , is a clear, colourless oil distilling at 252—256°. The *benzoyl* derivative distils at 210—215° under a pressure of 20 mm.

Dipentene, when treated in the same manner at 190—195°, yields a condensation product,  $C_{11}H_{18}O$ , distilling at 242—248° and having a sp. gr. = 0.9459 at 20°. Its *acetyl* derivative distils at 258—261°. Limonene also forms a condensation product,  $C_{11}H_{18}O$ , distilling at 246—250°, and having a sp. gr. = 0.9568 at 20°; its *acetyl* derivative boils at 259—263°.

J. J. S.

**Essential Oils.** By SCHIMMEL & Co. (*Chem Centr.*, 1898, ii, 984—985; from Schimmel and Co.'s Bericht, 1898, October).—The commercial oils of citronella comprise the following two groups: (1) oils which contain 80—90 per cent. of geraniol and citronellaldehyde, have a sp. gr. = 0.886—0.894 at 15° and a rotatory power =  $-0^{\circ} 34'$  to  $-2^{\circ} 20'$ , and (2) oils which contain 50—65 per cent. of geraniol and citronellaldehyde, have a sp. gr. = 0.896—0.919 at 15°, and a rotatory power =  $-7^{\circ} 10'$  to  $-20^{\circ} 37'$ . In one of the oils of the latter group having a sp. gr. = 0.915, large quantities of a camphor of specific rotatory power  $[\alpha]_D = -55^{\circ}$  were present and methyleugenol was also detected. The sp. gr. of a number of samples of dill oil

from Thuringian dill fruit varied from 0.899 to 0.911 and the rotatory power from  $+76^{\circ}$  to  $+79^{\circ}$ . Unlike the English and Spanish oils, they contained only a small quantity of phellandrene.

Three samples of eucalyptus oil from Portugal were examined. The first, prepared from *Eucalyptus rostrata*, had a pleasant odour and a high content of cineol; it was soluble in 2 parts of 70 per cent. alcohol, had a sp. gr. = 0.921, and a specific rotatory power at  $30^{\circ}$   $[\alpha]_D = -1^{\circ} 8'$ . The second, prepared from *Eucalyptus resinifera* (or *Eucalyptus rostrata* Schl.?) contained cineol and phellandrene; it was insoluble in 70 or 80 per cent. alcohol, had a sp. gr. = 0.893, and a specific rotatory power at  $30^{\circ}$   $[\alpha]_D = -17^{\circ} 8'$ . The third oil, prepared from *Eucalyptus obliqua* L'Herit, contained cineol and phellandrene, was soluble in an equal volume of 80 per cent. alcohol, had a sp. gr. = 0.914, and a specific rotatory power  $[\alpha]_D = -7^{\circ} 28'$ .

Portuguese oil of lavender, prepared from *Lavendula pedunculata* Cav., had an unpleasant odour and contained cineol and probably thujon; it was soluble in an equal volume of 80 per cent. alcohol, had a sp. gr. = 0.939, a specific rotatory power  $[\alpha]_D = -44^{\circ} 54'$ , and a content of ethers corresponding with 39 per cent. of linalylic acetate. Matico oils have recently been prepared which contain asarone in place of the easily crystallisable matico camphor, and also probably methyleugenol; they have a sp. gr. = 1.077 at  $15^{\circ}$  and a specific rotatory power  $[\alpha]_D = -0^{\circ} 25'$ .

Sandal wood oil, from *Santalum cygnorum* Miquel, has been recently distilled in Fremantle, West Australia. In order to test oil of spike for levorotatory turpentine oils, the authors recommend the use of Ladenburg's flasks and distil 5 c.c. from 50 c.c. of oil; the distillate should have about the same dextrorotatory power as the original oil.

In determining the point of solidification of aniseed oils, a slightly modified form of Beckmann's freezing point apparatus is used.

According to the authors, Indian geranium oil contains caproic acid, and at the most only traces of citronellol, but Flatau and Labbe's fatty acid,  $C_{14}H_{28}O_2$ , is not present in pure oils. Moreover, Flatau and Labbe's method of separating geraniol and citronellol does not yield a pure citronellol.

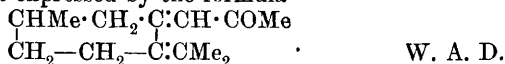
Fenchene, when treated with glacial acetic acid and sulphuric acid, is converted into an isomeride of fenchylic alcohol,  $C_{10}H_{18}O$ , which melts at  $61.5-62^{\circ}$ , and when oxidised yields a fenchone whose oxime melts at  $82^{\circ}$ .

In reply to Stiehl, the authors state that lemon grass oil always contains methylheptenone and geraniol.

E. W. W.

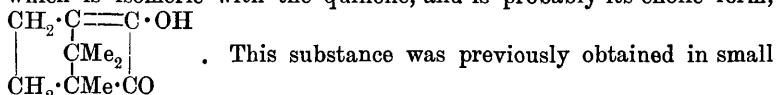
**Pulegenacetone.** By PHILIPPE BARBIER (*Compt. rend.*, 1898, 127, 870-872).—On warming a mixture of pulegone ( $1\frac{1}{2}$  mols.), ethylic acetoacetate ( $\frac{1}{2}$  mol.), and glacial acetic acid (100 grams) with fused zinc chloride (75 grams) for 10 hours on the water-bath and extracting with ether, a liquid is obtained which, after the removal of unchanged pulegone and ethylic acetoacetate, boils at  $148-153^{\circ}$  under a pressure of 8 mm., and solidifies in the receiver; on crystallising the product from light petroleum of very low boiling point, *pulegenacetone*,  $C_{15}H_{20}O$ ,

separates in beautiful prisms which melt at 72—73°. Its crystalline *oxime*,  $C_{13}H_{21}NO$ , melts at 134—135°, and yields a *benzoyl* derivative crystallising in transparent, yellow needles and melting at 178—179°. From its mode of formation, and the fact that it yields iodoform in presence of sodium hypobromite and potassium iodide, the structure of pulegenacetone is best expressed by the formula



**The Melting Points of Some Derivatives of Amidocamphor (Correction).** By OTTO MANASSE (*Ber.*, 1898, 31, 3260. Compare Abstr., 1893, i, 479).—The melting points have been redetermined with carefully purified substances. Formamidocamphor melts at 87° (formerly stated 76—77°); acetamidocamphor melts at 121—122° (formerly stated 108°); benzamidocamphor melts at 141° (formerly stated 140°).  
A. H.

**Reactions of Camphoquinone.** By OTTO MANASSE and ERNST SAMUEL (*Ber.*, 1898, 31, 3258—3260. Compare Abstr., 1898, i, 147).—When camphoquinone is treated in the cold with sulphuric acid containing 5 per cent. of sulphuric anhydride, a substance is produced which is isomeric with the quinone, and is probably its enolic form,



quantities by the action of ordinary sulphuric acid on the quinone, but a much larger yield is obtained by the use of the fuming acid. When boiled with dilute sulphuric acid, it is quantitatively converted into acetone and an *acid*,  $C_7H_{12}O_3$ , which melts at 50—51°, and is probably a methylhydroxycyclopentanecarboxylic acid. The study of this reaction is being pursued.  
A. H.

**Constitution of Camphoric Acid.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1897, [iii], 17, 990—998).—The author concludes from the work of Noyes and of Walker that camphoric acid is a derivative of succinic acid containing the group  $\cdot \text{CMe}(\text{COOH}) \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2$ , whilst its oxidation products indicate the presence of the group  $\text{:C} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{C:}$ ; he therefore regards it as 1:1:2-trimethylcyclopentane-2:3-dicarboxylic acid,  $\text{CH}_2 \begin{array}{l} \text{CMe}_2 \cdot \text{CMe} \cdot \text{COOH} \\ \text{CH}_2 - \text{CH} \cdot \text{COOH} \end{array}$ .

T. M. L.

**NOTE.**—This formula was suggested by W. H. Perkin, jun. (*Proc.*, 1896, 191), as an alternative to the 2:4-formula, but was rejected, in favour of the latter, in his recent paper (*Trans.*, 1898, 73, 798).

T. M. L.

**Glucosides containing Caffeine and Theobromine, obtained from Plants.** By C. SCHWEITZER (*Chem. Centr.*, 1898, ii, 217—218, from *Pharm. Zeit.*, 43, 380—381. Compare Hilger, *Pharm. Zeit.*, 38, 511).—When fresh kola nuts are extracted with chloroform, 0.613 per cent. of free caffeine, containing 1.2 per cent. of theobromine, is obtained. By treating the macerated nuts with 20 per cent. alcohol

and adding the filtrate to absolute alcohol, a ferment separates as a flocculent precipitate; kolanin is obtained from the alcoholic extract after removing the ferment and the theobromine, caffeine, sugar, salt, &c., by treating it with water containing alkali. When the alkaline extract is neutralised, the glucoside separates as a reddish, amorphous mass. By the action of the ferment or of boiling dilute sulphuric acid, kolanin yields glucose, caffeine, theobromine, and kola-red; from the quantities of the products obtained in the latter reaction kolanin may be regarded as formed by the combination of 1 mol. of kola-red with 3 mols. of glucose and 1 mol. of caffeine with elimination of 4 mols. of water, its composition would then be,  $C_{40}H_{56}N_4O_{21}$ . The fruit of *Theobroma Cacao* also contains theobromine and a ferment. To prepare the glucoside, cacaonin, the ferment is extracted with 20 per cent. alcohol, and the residue, after removing the fats with light petroleum, is treated with 90 per cent. alcohol. By the action of the ferment or of dilute sulphuric acid, cacaonin yields the same products as kolanin. The composition of cacaonin may perhaps be regarded as  $C_{60}H_{86}O_{15}N_4$ , which corresponds with that of a compound formed by the combination of 1 mol. of cacao-red,  $C_{17}H_{12}(OH)_{10}$ , with 6 mols. of glucose and 1 mol. of theobromine with loss of  $8H_2O$ . E. W. W.

**Two New Desmotroposantonins.** By AMERICO ANDREOCCHI and P. BERTOLO (*Ber.*, 1898, 31, 3131—3133).—Santonin has the following specific rotations,  $[\alpha]_D$ , in the solvents named; in nitric acid of sp. gr. 1.33,  $-246^\circ$  at  $30^\circ$ ; in sulphuric acid of sp. gr. 1.82,  $-409^\circ$  at  $27^\circ$ , of sp. gr. 1.68,  $-361^\circ$  at  $27^\circ$ ; in phosphoric acid of sp. gr. 1.697,  $-325^\circ$  at  $27^\circ$ .

When santonin is warmed with  $1\frac{1}{2}$  times its volume of dilute sulphuric acid at  $50-60^\circ$ , it is converted into *levodesmotroposantonin*,  $C_{15}H_{18}O_3$ . This melts at  $194^\circ$ , and has the specific rotation  $[\alpha]_D = -139^\circ$  at  $28^\circ$  in absolute alcoholic solution; reduction with zinc powder and acetic acid converts it into dextrosantonous acid; it yields a *monacetyl* derivative which melts at  $154^\circ$ , and has the specific rotation  $[\alpha]_D = -122.9^\circ$  at  $27^\circ$  in absolute alcoholic solution; when heated with ethylic iodide and sodium ethoxide, it forms an *ethyl* derivative, which melts at  $82^\circ$ , has the specific rotation  $[\alpha]_D = -129.3^\circ$  at  $27^\circ$ , shows the characters both of a phenol and of a lactone, and is reduced by zinc powder and acetic acid to dextroethylsantonous acid,  $C_{15}H_{19}O_2 \cdot OEt$ . This *levodesmotroposantonin* resembles the dextrorotatory isomeride melting at  $189^\circ$  in physical properties other than rotatory power, and an even closer resemblance exists between the acetyl and ethyl derivatives of these two substances; they unite to form racemic compounds.

*Racemic desmotroposantonin* is best obtained by hydrolysing the racemic acetyl derivative with caustic potash; it melts at  $198^\circ$ , its *acetyl* and *ethyl* derivatives at  $145^\circ$  and  $106^\circ$  respectively; zinc and acetic acid reduce it to racemic santonous acid. C. F. B.

**A New Crystalline Substance Present in Wormwood.** By ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1898, 127, 874—876).—On evaporating an alcoholic extract of *Artemisia Absinthium*, after removal of the absinthin, and treating the residue with amylic alcohol, a pale yellow solution is obtained from which, after two or

three days, straw-coloured, prismatic needles are deposited; after being recrystallised, the *substance* thus obtained melts at  $165^{\circ}$ , and has the composition  $C_{53}H_{51}O_{20}$  or  $C_{52}H_{51}O_{20}$ , a cyroscopic determination of the molecular weight confirming these formulæ. It is insoluble in water and ether, but dissolves in amylic alcohol, chloroform, acetone, and light petroleum; it differs from absinthin in possessing no bitter taste, is insoluble in dilute acids and alkalis, but dissolves unchanged in cold concentrated acids, although it is decomposed by them when warm; boiling concentrated alkalis decompose it, giving rise to resinous products. With its solution in acetic acid, bromine yields an unstable *compound*; ferric chloride gives a copious black precipitate, whilst iodine dissolved in aqueous potassium iodide produces a characteristic indigo-blue precipitate. The new principle of wormwood is not changed when boiled with potassium dichromate or lead peroxide in acetic acid solution; nascent hydrogen is also without action. When heated with lime, homologues of phenol are obtained. Acetic anhydride gives rise to a white *substance*, crystallising in leaflets, which contains  $C = 61.63, H = 5.29, O = 33.08$  per cent., melts at  $162-163^{\circ}$ , and does not yield acetic acid when heated with lime; the new substance differs from the compound from which it was prepared in its behaviour with ferric chloride and iodine, and appears to be formed by internal condensation.

W. A. D.

**Pyridine Derivatives from Ethylic Methylacetoacetate.** By A. SACHS (*Ber.*, 1899, 32, 61-64).—Ethylic methylacetoacetate, when treated with sodium ethoxide and trimethylenic bromide according to Lipp's method (*Abstr.*, 1897, i, 229), yields an oily mixture which cannot be hydrolysed by hydrochloric acid, but when boiled for 3 hours with potassium hydroxide (2.5 per cent.), yields ethylic alcohol, *methylacetobutylic alcohol*,  $CHMeAc \cdot [CH_2]_3 \cdot OH$ , and its *anhydride*,  $C_7H_{12}O$ , which are best separated by distillation under diminished pressure. The anhydride boils at  $37^{\circ}$  under 20 mm., or at  $131^{\circ}$  under atmospheric pressure, is a mobile oil with a strong odour of camphor, and when shaken for several days with 5 times its volume of water, yields methylacetobutylic alcohol. This is an oily liquid, practically without odour, sparingly soluble in water, and distilling at  $127^{\circ}$  under a pressure of 20 mm. When treated with hydrogen bromide, it yields the corresponding *bromide*, which distils at  $112^{\circ}$  under a pressure of 20 mm., is practically insoluble in water, and quickly undergoes decomposition. When the bromide (1 mol.) is left in contact with alcoholic ammonia (2 mols.) for 24 hours, the solution evaporated, and the residue treated with aqueous potassium hydroxide and distilled, 2:3-dimethyltetrahydropyridine,  $CH_2 \begin{smallmatrix} CMe:CMe \\ CH_2 \cdot CH_2 \end{smallmatrix} NH$ , is obtained as a liquid with an odour of pyridine, which readily turns brown on exposure to the air, is volatile with ether, boils at  $154-156^{\circ}$ , and is extremely difficult to dehydrate. The *hydrochloride* is extremely hygroscopic, the *picrate* crystallises in yellow needles melting at  $146^{\circ}$ , the *aurichloride*,  $C_7H_{14}NAuCl_4$ , melts at  $140^{\circ}$ , and is reduced when warmed with water at  $65^{\circ}$ . The *mercurichloride*,  $C_7H_{13}N, HCl + 5HgCl_2$ , is practically insoluble in cold water and melts at  $211^{\circ}$ .



Methylamine also reacts with the bromide, yielding 1 : 2 : 3-trimethyl-tetrahydropyridine,  $C_8H_{15}N$ , which distils at  $165-167^\circ$ , and has an extremely disagreeable odour; its *picrate* melts at  $152^\circ$ , and its *aurichloride* melts and decomposes at  $158^\circ$ .

A base of higher boiling point is also formed.

J. J. S.

### Synthetical Alkines of the Pyridine and Piperidine Series.

By ALBERT LADENBURG (*Annalen*, 1898, 304, 54—86. Compare Abstr., 1898, i, 687).—[With KRÜGEL].—1-Ethyl-2-pipecoleine,  $C_8H_{15}N$ , prepared by the action of ethylamine on  $\omega$ -bromobutyl methyl ketone, is a colourless, mobile oil which boils at  $163^\circ$ , and resinifies when exposed to air; it has the sp. gr. = 0.8907 at  $17.5^\circ$ , and the refractive indices  $n_D = 1.4861$  and  $n_F = 1.49427$ , whence the dispersion = 0.00817. The *platinochloride* forms rhombohedra, and melts at  $198-199^\circ$ ; the *mercurichloride* melts and decomposes at  $212-213^\circ$ .

1-Ethyl-2-pipecoline,  $C_5NH_5MeEt$ , obtained by reducing 1-ethyl-2-pipecoleine with tin and hydrochloric acid, boils at  $147-148^\circ$ , and has a sp. gr. = 0.8368 at  $17.5^\circ$ ; the refractive indices  $n_D = 1.4480$  and  $n_F = 1.4541$ , whence the dispersion = 0.00617. The *hydrochloride* is crystalline, but hygroscopic; the *aurichloride* and *mercurichloride* melt at  $108^\circ$  and  $209-210^\circ$  respectively.

N-Ethyl- $\alpha$ -pipecolyl- $\beta$ -alkine [2-methyl-3-hydroxymethyl-1-ethyl- $\Delta_2$ -tetrahydropyridine],  $OH \cdot CH_2 \cdot C_5NH_5MeEt$ , arises from the action of aqueous formaldehyde on the dilute solution of 1-ethyl-2-pipecoleine, and is colourless when freshly distilled, but rapidly becomes yellow, and finally brown; it boils at  $211^\circ$ , has a sp. gr. = 0.93965 at  $17.5^\circ$ , and the refractive indices  $n_D = 1.4626$  and  $n_F = 1.46864$ , whence the dispersion = 0.00604. The *platinochloride* melts at  $135-136^\circ$ , and decomposes at  $150^\circ$ ; the *aurichloride* crystallises from alcohol in rhombohedra, sinters at  $94^\circ$ , and melts at  $111^\circ$ .

N-ethyl- $\alpha$ -pipecolyl- $\beta$ -alkine [2-methyl-3-hydroxymethyl-1-ethylpiperidine],  $C_9H_{19}NO$ , prepared by reducing the foregoing base with sodium and alcohol, is a colourless, viscous liquid which boils at  $225.7^\circ$  (corr.), and has a sp. gr. = 0.9549 at  $17.5^\circ$ ; the refractive indices  $n_D = 1.4778$  and  $n_F = 1.4844$ , whence the dispersion = 0.0066. Di-ethylpipecolylalkinium [2-methyl-3-hydroxyethyl-1 : 1-diethylpiperidinium] iodide, obtained on gently heating an alcoholic solution of the alkine with ethylic iodide, crystallises in needles; the *platinochloride*, *aurichloride*, and *mercurichloride* of the chloride melt at  $190^\circ$ ,  $91-92^\circ$ , and  $148-149^\circ$  respectively.

1-Ethyl-2 : 3-ethylenepiperidine,  $C_9H_{17}N$ , is formed by heating the alkine with fuming hydrochloric acid at  $180-185^\circ$  during 2 hours; it has the odour of coniine, boils at  $178-180^\circ$ , and has a sp. gr. = 0.86818 at  $17.5^\circ$ . The *platinochloride*, *aurichloride*, and *mercurichloride* melt at  $162^\circ$ ,  $44-45^\circ$ , and  $82^\circ$  respectively.

[With ROSENZWEIG].—N-Ethyl- $\alpha$ -pipecolyl- $\beta$ -methylalkine [2-methyl-1-ethyl-3-hydroxyethyl- $\Delta^2$ -tetrahydropyridine],  $OH \cdot CHMe \cdot C_5H_6MeN \cdot Et$ , prepared by the action of acetaldehyde on 1-ethyl-2-pipecoleine, boils at  $106-107^\circ$  and  $221-223^\circ$  under pressures of 19—20 mm. and 754 mm. respectively; it has a sp. gr. = 0.94935 at  $21^\circ$ , and remains mobile at  $-20^\circ$ . The *hydrochloride* is crystalline, but very hygro-

scopic; the *platinochloride*, *mercurichloride*, and *picrate* melt at 167°, 116°, and 180° respectively.

*N-Ethyl- $\alpha$ -pipecolyl- $\beta$ -methylalkine* [2-methyl-1-ethyl-3-hydroxyethyl-piperidine],  $C_{10}H_{21}NO$ , arises from reduction of the alkine with sodium and alcohol; it is a colourless liquid having the odour of piperidine, boils at 230·5° under a pressure of 769 mm., and has a sp. gr. = 0·9417 at 30°. The *hydrochloride* is crystalline, but very hygroscopic; the *platinochloride*, *mercurichloride*, and *picrate* melt at 175—176°, 145°, and 145° respectively. The ethochloride forms a *platinochloride* and *mercurichloride* which melt at 205° and 130—131° respectively.

1-Ethyl-2:3-propylenepiperidine,  $C_{10}H_{19}N$ , prepared from the alkine by the action of fuming hydrochloric acid at 180—185°, boils at 196° under a pressure of 763 mm., and has a sp. gr. = 0·8772 at 23°; it is a yellow, viscous liquid having the odour of coniine. The *platinochloride*, *aurichloride*, and *mercurichloride* melt at 179°, 63°, and 84° respectively.

1-Ethyl-3-isopropylpiperidine,  $C_{10}H_{21}N$ , is probably the base obtained by reducing the alkine with tin and hydrochloric acid (compare *loc. cit.*), and forms a colourless, highly refractive liquid with the odour of coniine; it boils at 187—192° under a pressure of 743 mm., and has a sp. gr. = 0·8517 at 27°. The *aurichloride*, *mercurichloride*, and *picrate* melt at 73—74°, 84°, and 117° respectively. For comparison with ethylisconiine, 1:3-ethylpropylpiperidine has been prepared by eliminating ethylic chloride from diethylconium chloride. It boils at 185—193°, and has a sp. gr. = 0·8549 at 4°; a 30 per cent. solution in absolute alcohol gave  $\alpha = 8^\circ$  in a 0·5-decimetre tube. The *platinochloride* and *aurichloride* melt at 95° and 110° respectively.

[With THEODOR.]—1-Propyl- $\Delta^2$ -tetrahydropicoline,  $C_9H_{17}N$ , prepared from propylamine and bromobutyl methyl ketone, boils at 184° under a pressure of 768 mm., and has a sp. gr. = 0·8875 at 20°; the *platinochloride*, *aurichloride*, and *mercurichloride* melt at 180°, 58—59°, and 64° respectively.

1-Propyl-2-pipecoline,  $C_9H_{19}N$ , obtained by reducing 1-propyl-pipecoleine with tin and hydrochloric acid, is a colourless liquid with the odour of coniine, and melts at 167—167·5°. The *platinochloride*, *picrate*, and *mercurichloride* melt at 199—200°, 113°, and 142—143° respectively.

*N-Propyl- $\alpha$ -pipecolyl- $\beta$ -alkine* [2-methyl-3-hydroxymethyl-1-propyl- $\Delta^2$ -tetrahydropyridine],  $C_{10}H_{19}NO$ , is formed on treating 1-propyl-2-pipecoleine with formaldehyde; it is a limpid liquid which boils at 225° under a pressure of 758 mm., and has a sp. gr. = 0·9256 at 20°. The *picrate* crystallises from water in small, lustrous prisms, and melts at 147°.

*N-Propyl- $\alpha$ -pipecolyl- $\beta$ -alkine* [2-methyl-3-hydroxymethyl-1-propylpiperidine],  $C_{10}H_{21}NO$ , prepared by reducing the foregoing base with sodium and alcohol, boils at 233—234·5° under a pressure of 756·2 mm., and has a sp. gr. = 0·9376 at 20°; the *platinochloride* and *mercurichloride* melt at 184—185° and 78° respectively.

[With BRANDT.]—*N-Methyl- $\alpha$ -pipecolyl- $\beta$ -methylalkine* [1:2-dimethyl-3-hydroxyethyl- $\Delta^2$ -tetrahydropyridine],  $C_8NH_6Me_2 \cdot CHMe \cdot OH$ , obtained

from 1-methyl-2-pipecoleine and acetaldehyde, boils at 106—109° and 206—210° under pressures of 10 mm. and 752 mm. respectively, and has a sp. gr. = 0.9418 at 24°. The *aurichloride*, *platinochloride*, *mercurichloride*, and *picrate* melt at 127°, 175—177°, 158—165°, and 194—198° respectively.

N-Methyl- $\alpha$ -pipecolyl- $\beta$ -methylalkine [1 : 2-dimethyl-3-hydroxyethylpiperidine], formed on reducing the foregoing base with sodium and alcohol, crystallises in white needles melting at 30°; it boils at 227—229° (corr.) under a pressure of 756.8 mm., and has a sp. gr. = 0.9664 at 19°. The *platinochloride*, *mercurichloride*, and *picrate* melt at 197—198°, 169—171°, and 126—129° respectively.

1-Methyl-2 : 3-propylenepiperidine,  $C_9H_{17}N$ , is probably obtained by heating 1-methyl-2-pipecolyl-3-methylalkine with fuming hydrochloric acid at 180—190°; it is a limpid, colourless liquid, which boils at 179—184° under a pressure of 762.7 mm., and has a sp. gr. = 0.8797 at 20°. The *aurichloride*, *platinochloride*, *mercurichloride*, and *picrate* melt at 90—93°, 147—150°, 181—183°, and 108—110° respectively.

1-Methyl-3-isopropylpiperidine,  $C_9H_{19}N$ , is probably the base which is formed when the foregoing base is reduced with tin and hydrochloric acid; it is a colourless, mobile liquid, with the odour of piperidine, boils at 175—180° under a pressure of 743 mm., and has a sp. gr. = 0.8494 at 18°. The *aurichloride*, *platinochloride*, and *picrate* melt at 125—128°, 154—155°, and 162—163° respectively.

M. O. F.

**Aromatic Urethanes of Tetrahydroquinoline.** By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1898, 127, 868—870).—Tetrahydroquinoline interacts with phenolic carbonates in the same manner as piperidine, conicine, and piperazine (Abstr., 1898, i, 692), giving rise to aromatic urethanes; in preparing these, it is necessary to employ an excess of the base (4 mols.), which is boiled during 2 hours with the phenolic carbonate (1 mol.).

*Phenylic tetrahydroquinolineurethane*,  $C_9H_{10}N \cdot COOPh$ , prepared by this method from phenylic carbonate, separates from alcohol of 93° in white crystals, melts at 51—52°, distils unchanged at about 300°, and is easily soluble in the usual solvents; the corresponding *ortho-chloro-derivative*,  $C_9H_{10}N \cdot COO \cdot C_6H_4Cl$ , prepared from orthochlorophenylic carbonate, closely resembles it, and melts at 61°.

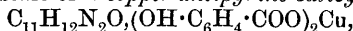
The *urethane*,  $C_9H_{10}N \cdot COO \cdot C_6H_4 \cdot OMe$ , prepared from guaiacol carbonate and tetrahydroquinoline, crystallises from alcohol in aggregates of hard needles radiating from centres, and melts at 69°.

$\alpha$ -Naphthylic and  $\beta$ -naphthylic tetrahydroquinolineurethanes, prepared from  $\alpha$ - and  $\beta$ -naphthylic carbonates, crystallise from alcohol, and melt at 73° and 118—119° respectively.

Attempts to prepare the tetrahydroquinolineurethanes derived from the cresols and thymol by the method given above, failed, mixed ethylic carbonates of the phenols alone being obtained (compare Cazeneuve and Morel, this vol., i, 29); the explanation of this behaviour is probably to be found in the difficulty with which the mixed alkylic and phenylic carbonates first formed undergo hydrolysis.

W. A. D.

**Double Salicylates of Metals and Antipyrine.** By M. C. SCHUYTEN (*Chem. Centr.*, 1898, ii, 704; from *Bull. Acad. roy. Belg.*, [iii], 35, 836—849. Compare *Bull. Acad. roy. Belg.*, [iii], 34, 933).—When copper sulphate (1 mol.) is added to a dilute solution of sodium salicylate (2 mols.) and antipyrine (1 mol.), rosette shaped clusters of green, rhombic crystals of a *copper antipyrine salicylate*,



separate; when more concentrated solutions are used, a flocculent precipitate is formed. The double salt is slightly soluble in water and alcohol, and melts and decomposes at  $192^\circ$ . As its solutions give the ordinary reactions of copper, the metal cannot be present in the salt as a complex ion.

Attempts to prepare double salicylates of antipyrine with silver, gold, and mercury failed. When a dilute solution of sodium salicylate and antipyrine is mixed with a solution of zinc chloride or zinc sulphate, a zinc antipyrine salicylate,  $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2 \cdot (\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{COO})_2\text{Zn}$ , separates after some time in colourless needles; this is slightly soluble in cold, but more soluble in warm, water, alcohol, and ether, rather soluble in cold chloroform, and melts and decomposes at  $75\text{--}76^\circ$ ; the aqueous solution has an acid reaction and gives the ordinary reactions of zinc salts. The cadmium salt,  $(\text{C}_{11}\text{H}_{12}\text{N}_2\text{O})_2 \cdot (\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{COO})_2\text{Cd}$ , prepared in a similar way to the above salts, crystallises in long needles, is slightly soluble in water, more easily in benzene and toluene, and melts and decomposes at  $95^\circ$ ; its aqueous solution also gives the reactions of cadmium salts.

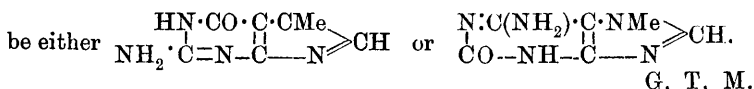
E. W. W.

**Homologues of Theobromine.** By HEINRICH BRUNNER (*Chem. Centr.*, 1898, ii, 474; from *Schweiz. Wochenschr. Pharm.*, 36, 303—304).—According to the author, there are two kinds of homologues of theobromine, the true homologues which crystallise with difficulty and melt above  $270^\circ$ , and derivatives of caffeine which crystallise easily in long needles and have lower melting points. The theobromine silver compound, when treated with methylic iodide, yields caffeine alone, but with ethylic iodide, a crystalline powder which melts above  $270^\circ$  is obtained, and also a crystalline isomeride which melts at  $165^\circ$ . The latter, which remains in the mother liquor, is identical with Van der Sloten's compound, whilst the former corresponds with Philips' preparation (this Jour., 1877, i, 93). Propylic iodide appears only to yield the microcrystalline modification with the higher melting point.

E. W. W.

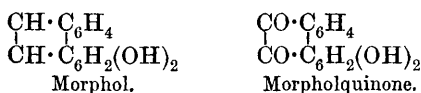
**Epiguanine (7-Methylguanine).** By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1898, 26, 389—394).—Epiguanine, obtained from urine, and formerly stated to have a composition corresponding with  $\text{C}_{10}\text{H}_{13}\text{N}_9\text{O}_2$  (Abstr., 1896, i, 92) is shown to be identical with 7-methylguanine (2-amido-6-oxy-7-methylpurine) synthesised by Fischer (Abstr., 1898, i, 98). On treatment with nitrous acid, the base is converted into heteroxanthine (7-methyl-xanthine),

$$\begin{array}{c} \text{HN} : \text{CO} \cdot \text{C} \cdot \text{NMe} \\ | \\ \text{OC} \cdot \text{NH} \cdot \text{C} \text{---} \text{N} \end{array} \text{---} \text{CH} ; \text{ therefore, 7-methylguanine may}$$



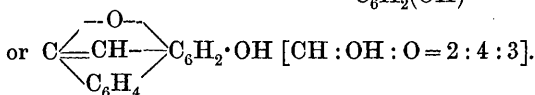
G. T. M.

**Non-nitrogenous Decomposition Products of Morphine.**  
 III. By EDUARD VONGERICHTEN (*Ber.*, 1898, 31, 2924—2925).—Acetylmethylmorpholquinone (Abstr., 1898, i, 98, 281) was digested with a solution of sodium methoxide in methyl alcohol; the methylmorpholquinone formed was liberated with sulphuric acid, suspended in water, and oxidised with excess of 4 per cent. potassium permanganate solution; from the filtered solution, the phenylhydrazone of phthalonic acid was obtained, and after acidifying and oxidising with excess of permanganate, phthalic acid was found to be present. In no experiment was any other than phthalic acid found, so that the two hydroxyl groups in morphol are attached to the same benzene nucleus; moreover, they are probably attached to adjacent carbon atoms, for Barth and Weidel showed some time ago that protocatechuic acid is formed when morphine is fused with potash. The following formulæ are, therefore, adopted.



C. F. B.

**Non-nitrogenous Decomposition Products of Morphine.**  
 By EDUARD VONGERICHTEN (*Ber.*, 1898, 31, 3198—3202. Compare Abstr., 1898, i, 98, 281).—Morphenol, when distilled with zinc dust in an atmosphere of hydrogen, yields phenanthrene; and its methylic ether, when reduced with sodium and alcohol, yields a *phenol* which crystallises in needles, but readily undergoes alteration when exposed to the atmosphere; its *acetyl* derivative could not be obtained in a crystalline form, but when oxidised with an acetic acid solution of chromic anhydride, it gave acetylmethylmorpholquinone; a *benzoylmethylmorpholquinone* melting at 228° has been obtained by treating the crude phenol with benzoic chloride and oxidising. The formula suggested for morphenol is  $\text{O} \begin{array}{c} \diagup \text{C} = \text{CH} \\ | \\ \text{C}_6\text{H}_2(\text{OH}) \end{array} \diagdown \text{C}_6\text{H}_4$  [C : OH : O = 2 : 4 : 5]



J. J. S.

**Thebaine.** By MARTIN FREUND [and CARL HOLTHOF] (*Ber.*, 1899, 32, 168—196. Compare Abstr., 1897, i, 495).—*Methebenine*,  $(\text{OMe})_2 \cdot \text{C}_{16}\text{H}_{11} \cdot \text{O} \cdot \text{NHMe}$ , obtained by heating thebaine (10 grams), during 2—3 hours at 100°, with methylic alcohol (15 c.c.) mixed with an equal volume of the alcohol which has been saturated with hydrogen chloride, sinters at 155°, melts at 165—167°, and is somewhat sparingly soluble in alcohol. The *hydrochloride* crystallises in aggregates of needles and melts at 245°; the *hydriodide* separates from dilute alcohol in rhombic plates, sinters at 190°, and melts at 195—198°. The *diacetyl* derivative crystallises from absolute alcohol in snow-white

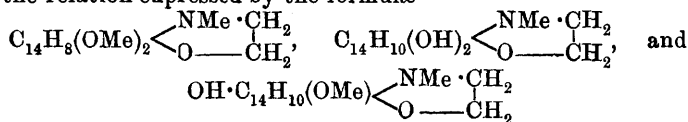
needles, and melts at  $176^{\circ}$ ; the *methylmethebenine methiodide*, produced by the action of methylic iodide in excess, forms microscopic prisms and melts at  $215^{\circ}$ . Methebenine is the methylic ether of thebenine, and the latter substance is obtained from it when the hydrochloride is heated with 20 per cent. hydrochloric acid. *Methebenol*,  $C_{16}H_{10}O(OMe)_2$ , is the result of eliminating hydrogen iodide and trimethylamine from the methinemethiodide by the agency of 15 per cent. caustic potash; it separates from glacial acetic acid in greyish crystals and melts at  $133-134^{\circ}$ . It is identical with the substance obtained from thebenol and methylic iodide (*loc. cit.*).

*Ethebenine*,  $OMe \cdot C_{16}H_{11}O(OEt) \cdot NHMe$ , is produced under conditions similar to those observed in the preparation of methebenine, ethylic alcohol being used instead of methylic alcohol; the *hydrochloride* melts at  $248^{\circ}$ , and the *hydriodide*, which crystallises from water in highly refractive, rhombic plates containing  $1H_2O$ , sinters at  $200^{\circ}$  and melts at  $206-207^{\circ}$ . The *diacetyl* derivative melts at  $163^{\circ}$ , and the *methylethebenine methiodide*, which crystallises in minute, six-sided plates, sinters at  $210^{\circ}$  and melts at  $215^{\circ}$ . *Ethebenol*,  $OEt \cdot C_{16}H_{10}O \cdot OMe$ , produced when the methinemethiodide is treated with boiling alkali, crystallises from glacial acetic acid in small, rhombic plates, and melts at  $103-105^{\circ}$ ; it is also obtained from thebenol and ethylic iodide in presence of sodium ethoxide.

*Prothebenine*,  $OMe \cdot C_{16}H_{11}O(OPr) \cdot NHMe$ , prepared from thebaine and propylic alcohol under the influence of hydrogen chloride, sinters at  $167^{\circ}$  and melts at  $172-173^{\circ}$ ; the *hydrochloride*, which crystallises in microscopic, six-sided leaflets, sinters at  $215^{\circ}$  and melts at  $220-221^{\circ}$ , whilst the *hydriodide* forms rhombic leaflets, softens at  $210^{\circ}$ , and melts at  $212-213^{\circ}$ . The *methylprothebenine methiodide* separates from dilute alcohol in microscopic, six-sided plates and melts at  $202^{\circ}$ . *Prothebenol*,  $OPr \cdot C_{16}H_{10}O \cdot OMe$ , obtained by the action of boiling caustic potash on the methinemethiodide, crystallises from glacial acetic acid in rhombic plates, softens at  $99^{\circ}$ , and melts at  $103-105^{\circ}$ ; it is also produced when thebenol is heated with propylic iodide and alcoholic sodium ethoxide.

Morphothebaine,  $C_{18}H_{19}NO_3$ , is the base obtained by the action of concentrated hydrochloric or hydrobromic acid on thebaine (compare Howard, *Abstr.*, 1884, 1201); the formula,  $C_{17}H_{17}NO_3$ , ascribed to it by Howard, is not confirmed by the author, who finds that one of the two methoxylic groups which occur in the original alkaloid remains intact. Morphothebaine crystallises from methylic alcohol in beautiful, bluish crystals belonging to the rhombic system. The hydrochloride, hydrobromide, and hydriodide melt at  $256-260^{\circ}$ ,  $270-275^{\circ}$ , and  $243-244^{\circ}$  respectively; the *triacetyl* derivative, regarded by Howard as the acetyl derivative, melts at  $193-194^{\circ}$ , whilst the *methiodide* crystallises in quadratic plates and melts at  $221-222^{\circ}$ .

The fact that thebaine, morphine, and codeine stand to one another in the relation expressed by the formulæ



respectively, suggested the possibility of arriving at the dimethylic ether of morphine or the methylic ether of codeine by addition of two hydrogen atoms to thebaine. This prospect, however, has not been realised.

*Dihydrothebaine*,  $C_{16}H_{14}O(OMe)_2 \cdot NHMe$ , prepared by reducing thebaine in alcoholic solution with sodium, crystallises from a mixture of benzene and petroleum in minute, quadratic prisms, and melts at  $154^\circ$ . The *methiodide* crystallises from ethylic alcohol in four-sided prisms which contain 1 mol. of the solvent and melt at  $155-160^\circ$ ; a similar form, containing 1 mol. of the solvent, separates from methylic alcohol, whilst water deposits the substance in minute needles melting at  $75-80^\circ$ , and containing  $3H_2O$ .

*Isodihydrothebaine hydriodide*,  $OH \cdot C_{16}H_{13}ONMe_2 \cdot OMe, HI$ , obtained by the action of sulphurous acid on the methiodide of dihydrothebaine, crystallises from hot water and melts at  $230-235^\circ$ ; the *base* crystallises from benzene and melts at  $138^\circ$ , whilst the *methiodide* melts at  $210-215^\circ$ .

*Isocodeine*,  $C_{18}H_{21}NO_3$ , is the name given by the author to a substance produced when dihydrothebaine is dissolved in cold, dilute hydrochloric acid; it is a snow-white, amorphous powder which melts at  $70-80^\circ$ .  
M. O. F.

**Brucine.** By NICOLA MOUFANG and JULIUS TAFEL (*Annalen*, 1898, 304, 24-49).—The authors confirm the empirical formula,  $C_{23}H_{26}N_2O_4$ , now ascribed to brucine, and although the alkaloid usually contains  $4H_2O$  when crystallised from water, have obtained a form from this solvent containing  $2H_2O$ ; the same modification is produced on crystallising brucine from alcohol.

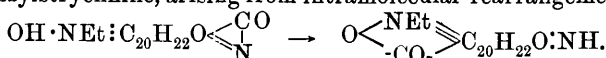
*Brucinic acid*,  $NH \cdot C_{20}H_{20}NO(OMe)_2 \cdot COOH$ , prepared by heating brucine with alcoholic sodium ethoxide at  $80^\circ$ , forms a crystalline powder containing  $1H_2O$ , and melts and decomposes at  $245^\circ$ ; it dissolves in dilute mineral acids, which converts it into salts of brucine. Chromic acid and ferric chloride develop a transitory green coloration, and concentrated nitric acid gives a yellowish-red solution. The nitrosamine yields a *hydrochloride*, which crystallises from warm water in small needles, and melts indefinitely at  $236^\circ$ . The *methiodide*, which is almost insoluble in cold water, contains  $1H_2O$ , and melts and decomposes at  $218^\circ$ . The *methylbetaine (methylbrucine)*,  $C_{24}H_{30}N_2O_5$ , prepared by the action of moist silver oxide on the methiodide of brucinic acid, forms yellow crystals containing  $4H_2O$ , which is removed at  $105^\circ$ ; it melts and decomposes at  $276^\circ$ .

*Nitrobrucine hydrate*,  $C_{21}H_{21}N_2O_3(OMe)_2 \cdot NO_2$ , obtained by heating brucine with 5 per cent. nitric acid in a reflux apparatus, is precipitated by sodium acetate from aqueous solutions in lustrous, golden leaflets containing water of crystallisation, which is removed at  $100^\circ$ ; it chars without melting when strongly heated. It is readily dissolved by dilute acids and by caustic alkalis; the solution in alkali carbonates is golden-yellow, becoming brown on treatment with caustic soda, whilst the solution in dilute ammonia also becomes brown when boiled. The *platinochloride* is crystalline, and the *mercurichloride* amorphous.

*Bidemethylnitrobrucine hydrate*,  $C_{21}H_{21}N_2O_3(OH)_2 \cdot NO_2$ , prepared

by the action of caustic soda on the nitrate (see below), is precipitated by acetic acid from alkaline solutions in reddish-yellow leaflets containing  $2\text{H}_2\text{O}$ , which is lost at  $105^\circ$ . The *nitrate* (cacothelin), obtained by heating brucine with 10 per cent. nitric acid at  $60\text{--}70^\circ$ , is an orange-coloured, crystalline powder, which becomes brown when exposed to light. The *hydrochloride* is crystalline, and dissolves in 45 parts of boiling water. M. O. F.

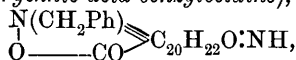
**Ethylstrychnine and Benzylstrychnine.** By NICOLA MOUFANG and JULIUS TAFEL (*Annalen*, 1898, **304**, 49—54. Compare Abstr., 1891, 1262).—The alkaline solutions obtained on treating strychnine ethiodide and benzylic chloride with moist silver oxide have been regarded by How and Garzarolli respectively as containing the corresponding ammonium bases; the products are, however, ethylstrychnine and benzylstrychnine, arising from intramolecular rearrangement, thus,



*Ethylstrychnine* (*strychnic acid ethylbetaine*),  $\text{O} \begin{array}{c} \diagup \text{NEt} \\ \diagdown \text{CO} \end{array} \text{C}_{20}\text{H}_{22}\text{O} : \text{NH}$ ,

is prepared by gently heating strychnine ethiodide with silver sulphate and water, and boiling the filtrate with excess of barium hydroxide for a few minutes; it crystallises from water in long, colourless needles containing  $4\text{H}_2\text{O}$ , and melts somewhat indefinitely at  $260^\circ$ . The behaviour of ethylstrychnine towards oxidising agents resembles that of the lower homologue.

*Benzylstrychnine* (*strychnic acid benzylbetaine*),



crystallises from hot water in colourless needles containing  $9\text{H}_2\text{O}$ ; it melts at about  $220^\circ$ , and dissolves in about 10 parts of boiling water. Its behaviour towards oxidising agents resembles that of the foregoing substance. M. O. F.

**Conversion-Temperature of Normal Strychnine Tartrate.** By ALBERT LADENBURG and GUIDO DOCTOR (*Ber.*, 1899, **32**, 50—57. Compare Abstr., 1898, i, 707).—The sp. gr. of the three normal strychnic salts have been obtained by the aid of the pycnometer and benzene of sp. gr. =  $0.86842$  at  $20^\circ/4^\circ$ , and equations for determining the rotatory power of solutions of different strengths have also been calculated.

	Sp. gr.	$[\alpha]_D^{20}$ .
1. Racemate .....	1.36653	$-31.87924 + 3.7487 p$ .
2. <i>l</i> -Tartrate .....	1.3405	$-31.36342 + 1.3564 p$ .
3. <i>d</i> -Tartrate .....	1.43218	$-20.60725 + 0.9367 p$ .

*p* denotes the percentage of anhydrous salt in the solution, and the equation holds good for concentrations between  $p=0.5$  and  $p=2$  per cent. The rotatory power rapidly diminishes on dilution, especially in the case of the racemate. The rotation for the racemate agrees only with that for equal quantities of the *d*- and *l*-tartrates calculated from 2 and 3, between the concentrations  $p=1.82$  and



$p = 1.88$ . The racemate is stable at the ordinary temperature, and at all temperatures below  $30^{\circ}$ .

Several of van't Hoff's methods have been adopted to determine the temperature at which the racemate becomes converted into the corresponding tartrates. The dilatometric method gave no definite results; a study of the solubility curves of mixtures of the tartrates and of the racemates indicated that at about  $30^{\circ}$  they crossed, and this would give the temperature of conversion at about  $30^{\circ}$ . Somewhat more correct results were obtained with the differential tensimeter, and the temperature was found to be  $29.5^{\circ}$ . It is pointed out that the usual conception, that a racemic acid, by the addition of an optically acid base, is directly resolved into salts of the two optically active acids, is erroneous. A partially racemic salt is first formed, and whether this or the salts of the two optically active acids crystallise out is merely a question of the temperature of conversion.

J. J. S.

**Alkaloid similar to Strychnine found in a Corpse.** By MECKE and WIMMER (*Chem. Centr.*, 1898, ii, 111; from *Pharm. Zeit.*, 43, 300—301).—The alkaloid which the authors have obtained from a corpse forms white, nodular crystals, and its hydrochloride, feathery, crystalline tufts. The alkaloid gives the same reactions as strychnine with picric acid, potassium dichromate and sulphuric acid, tannin, potassium ferricyanide, potassium thiocyanate, and nitric acid. The residue obtained after evaporating with chlorine water gives a dirty green coloration with ammonia. With Fröhde's reagent, the alkaloid gives first a dirty violet, then an olive, and, finally, a green coloration; with sulphuric acid, a yellow passing through cherry-red to rose-coloured, and with Erdmann's reagent, a yellow coloration. It has only a slightly bitter taste, and showed no physiological action on frogs.

E. W. W.

**Derivatives of Tropine.** By A. F. P. VAN SON (*Chem. Centr.*, 1898, ii, 665—666 and 889—890; from *Ned. Tijdsch. Pharm.*, 10, 242—257, 282. Compare *Abstr.*, 1898, i, 282).—By the action of a solution of silver nitrate on tropine iodide hydriodide,  $C_8H_{14}IN, HI$ , in the cold, 1 atom of iodine is removed, but the second iodine atom is only attacked when the mixture is kept warm for a long time. According to the author, the hydriodide melts at  $205^{\circ}$ — $206^{\circ}$  (Ladenburg  $115^{\circ}$ ). *Tropine iodide hydrochloride*,  $C_8H_{14}IN, HCl$ , prepared by treating the hydriodide with moist silver chloride, crystallises from absolute alcohol in colourless plates and melts at  $182^{\circ}$ . The *aurochloride*,  $C_8H_{14}IN, HAuCl_4$ , forms yellow, star-shaped crystals, and melts at  $167^{\circ}$ — $168^{\circ}$ ; the *platinochloride*,  $(C_8H_{14}IN)_2, H_2PtCl_6$ , crystallises in brown, star-shaped prisms, and melts at  $200^{\circ}$ ; the *mercurichloride*,  $C_8H_{14}IN, HHgCl_3$ , crystallises in long, branched needles and melts at  $140^{\circ}$ — $141^{\circ}$ . *Tropine bromide hydrobromide* is prepared by heating tropine at  $170^{\circ}$ — $180^{\circ}$  with 3—4 times its weight of hydrobromic acid solution saturated at  $0^{\circ}$ ; it crystallises from alcohol in colourless, star-shaped crystals, melts at  $216^{\circ}$ — $217^{\circ}$ , is easily soluble in water, slightly in alcohol, and insoluble in ether. The *hydrochloride of the bromide* crystallises in large, colourless prisms, melts at  $204^{\circ}$ — $205^{\circ}$ , is easily soluble in water, and insoluble in ether; the

*aurichloride* crystallises in yellow needles, melts at  $170^{\circ}$ , and is easily soluble in water; the *platinochloride* crystallises in long, yellow needles, melts at  $218-220^{\circ}$ , and is easily soluble in water; the *mercurichloride* crystallises in white, feather-like crystals and melts at  $165^{\circ}$ . The author was unable to prepare tropine chloride corresponding with the above bromide and iodide, in a pure state, but analysis of its *aurichloride* indicated the composition  $C_8H_{14}ClN, HAuCl_4$ ; it crystallises in yellow, feather-like crystals, and melts at  $204-206^{\circ}$ ; the *platinochloride* melts at  $226-227^{\circ}$ . By the action of silver chloride in tropinethylene bromide, tropinecholine chloride is formed. Its *aurichloride* crystallises in lustrous plates and melts at  $206-207^{\circ}$ , and its *platinochloride* forms prismatic crystals and melts at  $217^{\circ}$ ; both compounds are anhydrous.

E. W. W.

**Datura Alba and Hyoscine.** By OSWALD HESSE (*Annalen*, 1898, 303, 149—165).—The presence of hyoscine in the blossoms of the Chinese *Datura alba* has been observed by Browne, who ascribed to the alkaloid the empirical formula given by Ladenburg, namely,  $C_{17}H_{23}NO_3$ . The author, having previously shown that the composition is probably  $C_{17}H_{21}NO_4$ , has examined the alkaloid from the source indicated, and considers that the result confirms his original view.

Hyoscine is amorphous, and dissolves very readily in cold water; potassium hydrogen carbonate precipitates it unchanged from solutions of the hydrobromide. Under conditions described in the paper, hyoscine is not converted into atropine by the agency of silver oxide or caustic soda.

M. O. F.

**Laurotetanine: the Alkaloid of the Bark of Tetranthera Citrata.** By J. D. FILIPPO (*Arch. Pharm.*, 1898, 236, 601—622).—Laurotetanine,  $C_{19}H_{23}NO_5$ , was extracted from the bark of *Tetranthera citrata* (*Litsaea citrata*) by Greshoff's method, 20 kilograms of the bark yielding 50 grams of the alkaloid. It crystallises from ether in almost colourless groups of needles, melts at  $134^{\circ}$ , has a bitter, somewhat burning, taste, and is almost insoluble in water, ether, and benzene, but readily soluble in alcohol, chloroform, acetone, and ethylic acetate. Its alcoholic solution has an alkaline reaction. It gives characteristic colour reactions with concentrated nitric and sulphuric acids, is easily decomposed, and is especially characterised by its strongly reducing properties. The *aurichloride* is an unstable, amorphous, yellow precipitate; the *platinochloride* forms small, reddish-yellow crystals; the *hydrochloride*,  $C_{19}H_{23}NO_5, HCl + 6H_2O$ , crystallises in thick needles melting at  $46^{\circ}$ , the dried substance decomposes without melting at  $230^{\circ}$ ; the *hydrobromide*,  $C_{19}H_{23}NO_5, HBr + 2H_2O$ , forms colourless needles; the *hydriodide*,  $C_{19}H_{23}NO_5, HI + 2H_2O$ , crystallises in groups of pale yellow needles; the *sulphate*,  $(C_{19}H_{23}NO_5)_2H_2SO_4 + 5H_2O$ , forms small, prismatic crystals, and the *picrate* crystallises in small, yellow needles decomposing at  $150^{\circ}$ , without melting.

When heated with methylic iodide, the alkaloid is converted into the hydriodide, but with ethylic iodide, *ethyl-laurotetanine hydriodide*,  $C_{19}H_{22}EtNO_5, HI$ , is formed, crystallising from water in small needles melting at  $212^{\circ}$ , and proving that the alkaloid is a secondary base.

By the action of sodium carbonate on the hydriodide, *ethyl-laurotetanine* is obtained, crystallising from glacial acetic acid in small needles melting at 127—130°. It has a strong reducing reaction, but owing to scarcity of material its properties could not be thoroughly investigated.

*Laurotetaninephenylthiocarbamide*,  $\text{NHPh} \cdot \text{CS} \cdot \text{NC}_{19}\text{H}_{22}\text{NO}_5$ , prepared by the action of phenylthiocarbimide on the alcoholic solution of the base, crystallises from alcohol in needles melting at 211—212°. Ethyl-laurotetanine is not acted on by phenylthiocarbimide.

Hydroxylamine and phenylhydrazine are without action on the alkaloid, which was shown to contain three methoxy-groups. By the action of benzoic chloride, a crystalline substance is obtained melting at 194°, and is probably a *dibenzoyl* derivative, although this has not so far been definitely proved.

From experiments made on frogs, the alkaloid acts as a cramping poison, producing reflex action of the central nerve system.

A. W. C.

**Diastase.** By WALTER J. SYKES and H. NEVILLE HUSSEY (*J. Fed. Inst. Brew.*, 1898, 4, 527—544).—In order to avoid the employment of alcohol in the preparation of diastase from malt, the authors used saturated solutions of sodium sulphate and magnesium sulphate; the precipitates, however, obtained in this way were found not to be very active. From barley, an active diastase was obtained by precipitation with a saturated solution of ammonium sulphate. Experiments made with the object of splitting up diastase by means of fractional precipitation with ammonium sulphate gave negative results. The precipitate given by magnesium sulphate was found to be capable of inverting cane-sugar, showing that some, at least, of the invertase of the malt is thrown down with the diastase.

A. C. C.

**Presence of a Soluble Proteolytic Ferment in Certain Fungi.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1898, 127, 666—669).—It has appeared from previous researches that the only fungus capable of producing a proteolytic enzyme is *Aspergillus niger*, an aqueous maceration of which acts on fibrin and albumin in the same manner as an aqueous solution of trypsin. It is now shown, however, that twenty out of twenty-six fungi examined, when macerated with sand and water containing chloroform, yield a solution which, after filtration, is capable of almost completely digesting casein, yielding peptones together with tyrosine. The above-mentioned fungi are thus capable of elaborating an enzyme analogous to, if not identical with, trypsin; it is destroyed when its solution is boiled, although not affected by the presence of chloroform. The casein employed was in the form of milk from which the fats had been removed by means of alcohol-ether containing ammonia; the ferment thus acted in presence of small quantities of alcohol and ammonia.

W. A. D.

**Laccase: A New Oxidising Soluble Ferment.** By GABRIEL BERTRAND (*Ann. Chim. Phys.*, 1897, [vii], 12, 115—140).—This paper refers to work already published (compare Abstr., 1895, i, 386; 1896, i, 534, ii, 61, 571; 1897, ii, 117; 1898, i, 53, ii, 128).

G. T. M.

**Oxydases and the Guaiacum-Reaction.** By J. GRÜSS (*Chem. Centr.*, 1898, ii, 366; from *Ber. Deutsch. bot. Ges.*, 16, 129—139).—The author distinguishes three oxydases and describes their distribution in plants. *α-Oxydase* is soluble in glycerol and is partially precipitated from its solution by lead acetate without decomposing. *β-Oxydase* is also soluble in glycerol and is precipitated by alcohol and ether; it can be detected in potatoes by leaving the resting tubers in alcohol for several days, or by heating them with alcohol at 50—53° for 10 minutes. *γ-Oxydase* is not decomposed even by boiling alcohol, and is detected by the blue coloration obtained with guaiacum-hydrogen peroxide after boiling the specimen to be tested with alcohol for  $\frac{1}{4}$ —1 hour.

E. W. W.

**Colouring Matter of Bile.** By WILLIAM KÜSTER (*Zeit. physiol. Chem.*, 1898, 26, 314—337. Compare Abstr., 1897, i, 647).—The author has repeated his previous experiments with larger quantities of materials, and gives a detailed account of the preparation of crystallised bilirubin,  $C_{16}H_{18}N_2O_3$ , and its subsequent oxidation into biliverdin,  $C_{16}H_{18}N_2O_4$ . A yield of 20 per cent. of biliverdic acid,  $C_8H_8NO_4$ , is obtained when biliverdin is oxidised with a hot acetic acid solution of sodium dichromate. The *silver*, *calcium*, and *ammonium* salts of this acid all contain  $1H_2O$ ; the basic *cadmium* salt crystallises in aggregates of needles. When titrated with cold alkali, biliverdic acid is monobasic, but slowly changes into a dibasic compound, and on boiling with caustic soda it evolves ammonia and becomes converted into the lactone of tribasic hæmatic acid,  $C_8H_8O_5$ . This hydrolysis indicates the close relationship existing between the blood and bile-colouring matters; the molecules of bilirubin and hæmatin both contain complexes from which the substance  $C_8H_8O_5$  can be obtained, although the yield from biliverdin is only half that from hæmatin.

G. T. M.

**Bromo-proteinchrome.** By D. KURÁEFF (*Zeit. physiol. Chem.*, 1899, 26, 501—512).—Among the products of digestive proteolysis, the one which gives a colour with bromine has hitherto been little investigated chemically. Under some circumstances, a red, under others a black, under others, again, a bluish-violet product is obtained. The osmotic properties of these substances are on about the same level as those of peptone. Elementary analyses are given, and the substances contain carbon, hydrogen, bromine, nitrogen, sulphur, and oxygen, the percentage of bromine varying from 24 to 34. The coloured products are believed to be bromine derivatives of albumoses.

W. D. H.

**Union of Iodine with Crystallised Egg-albumin and Serum-albumin.** By D. KURÁEFF (*Zeit. physiol. Chem.*, 1899, 26, 462—486).—Crystalline albumin was prepared according to the recognised methods, but without the addition of acid. Iodine was added in a potassium iodide solution, or as a mixture of iodide and iodate of potassium, the precipitate being dissolved in weak ammonia and again precipitated by acids. Its properties were like those of Hofmeister's iodalbunin; the percentage of iodine in the serum-albumin preparation varied from 9.86 to 12.28, the average in ten

preparations being nearly 12. From the analyses, the empirical formula,  $C_{450}H_{693}I_{11}N_{116}S_4O_{132}$ , may be deduced. The percentage of iodine in the preparation from egg-albumin is less. W. H. D.

**Decomposition of Albumin by Hydrochloric Acid. II.** By RUDOLF COHN (*Zeit. physiol. Chem.*, 1899, 26, 395—410. Compare Abstr., 1896, i, 658; 1898, i, 343).—In previous work, the author succeeded in obtaining products which accounted for 91 per cent. of the casein originally taken, and by more careful analysis he has now brought this number up to 97·8; of this, tyrosine accounts for 3·5 and leucine for 31 per cent. Glutamic acid is a large constituent of the products obtained, whilst pyridine derivatives are only present in small quantity.

Benzoic chloride is a good precipitant for lysine.

Horny material was subjected to similar treatment; the most striking point in the results is the high percentage of tyrosine obtained. W. D. H.

**Oxidation of Albumin with Permanganate.** By RICHARD BERNERT (*Zeit. physiol. Chem.*, 1898, 26, 272—307. Compare Maly, Abstr., 1885, 824; 1888, 1120; and 1889, 629).—When oxyprotosulphonic acid, obtained from egg-albumin by oxidation with potassium permanganate, is subjected to Pick's method of fractional precipitation with ammonium sulphate (Abstr., 1898, i, 288 and 608), it is separated into two fractions, whereas that obtained from crystallised serum-albumin appears to be homogeneous. Leucine and aspartic and melanoidic acids are obtained on hydrolysing oxyprotosulphonic acid with concentrated hydrochloric acid, but tyrosine and glutamic acid cannot be detected among the products of reaction. If, as Maly assumed, the oxidation of albumin to oxyprotosulphonic acid is effected without fission of the molecule, this action should not be attended by the formation of bye-products; it is found, however, that considerable quantities of substances resulting from the decomposition of albumin are simultaneously produced, and the author suggests that oxyprotosulphonic acid may differ considerably in molecular complexity from the parent substance, and that the hydrolytic action of the alkali set free during oxidation must also be taken into account. The mother liquors from the oxyprotosulphonic acid are neutralised with ammonia and concentrated until potassium sulphate separates; the filtrate, when treated with ammonium sulphate, yields a precipitate which is redissolved in water and fractionated by means of the same reagent into three albumoses. From the final mother liquors, two peptones are obtained, which differ in their solubility in alcohol. A table is given showing the behaviour of these albumoses and peptones towards the usual reagents for proteid substances. Like oxyprotosulphonic acid, these five substances yield neither scatole nor indole on fusion with potash, they contain no loosely combined sulphur as indicated by the lead acetate test, and they give negative results with Millon's, Adamkiewicz's, and the xanthoproteic reactions. The fatty acids present in the mother liquors, after precipitating the albumoses, are separated by distillation with steam and converted into their ethylic salts; acetic and propionic acids are thus identified, whilst the amount of butyric

acid obtained is so small that it is impossible to determine whether it is the normal or iso-compound. The bases, obtained by precipitation with phosphotungstic acid, are histidine and arginine, together with a compound probably identical with lysine. The author finds that Maly's peroxyprotoic acid, produced by the oxidation of oxyproto-sulphonic acid, is not homogeneous, but consists of two substances giving different figures on analysis; one of these is precipitated by mercuric acetate, and yields leucine, pyridine, acetic and butyric acids, but no trace of pyrroline or glutamic acid on hydrolysis with barium hydroxide, the other substance is precipitated by lead acetate, and when hydrolysed gives leucine, benzaldehyde, benzoic, acetic, propionic, and butyric acids; neither amidovaleric nor isoglyceric acids, obtained by Maly under these conditions, could be detected among the products.

G. T. M.

**The Albumoses of Witte's Peptone.** By HUGO SCHRÖTTER (*Zeit. physiol. Chem.*, 1898, 26, 338—342).—The author refers to his previous work on the subject (*Abstr.*, 1894, i, 215; 1896, i, 112, 515; 1898, i, 610), and complains of the scant notice it has received in recent publications by others.

W. D. H.

## Organic Chemistry.

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**Solubility of Organic Compounds in Water.** By WILHELM VAUBEL (*J. pr. Chem.*, 1899, [ii], 59, 30—45).—The solubility of gaseous aliphatic compounds in water is greatest when a triple bond is present and least when only single bonds occur; as a rule, it decreases with increase of the percentage of carbon. As regards liquid and solid compounds, both aliphatic and aromatic, it is only the oxygen derivatives which are appreciably soluble in water, and their solubility is less the greater the percentage of carbon. In the case of the monhydric alcohols and monobasic acids, solubility practically ceases when 5 or 6 atoms of carbon are present, a number which may be conceived as arranged in a ring without too great a displacement from their normal positions. Incidentally, it was found that aqueous solutions of aldehyde have a maximum density corresponding with about 20 per cent. of aldehyde. In the oxalic acid series, the solubility alternately rises and falls, as does the melting point; it is large when an odd number of carbon atoms is present, comparatively small when the number is even. The author seeks to explain this by means of his space formulæ (compare *Abstr.*, 1898, i, 129); it is to the presence of the COOH groups that the solubility must be attributed, and in the acids with an even number of carbon atoms these groups lie towards opposite sides of the molecule, and so tend to neutralise each other, whilst they lie towards the same side, and, therefore, reinforce each other, when the number of carbon atoms is odd. In harmony with this view is the fact that fumaric acid is but slightly soluble in water, whilst maleic acid is very soluble. In a similar fashion, it is sought to explain the smaller solubility of paradihydroxybenzene, diamidobenzene, and benzenedicarboxylic acid, as compared with the meta-isomerides; further, ortho-derivatives are compared with acetylenedicarboxylic acid. The influence of the nature and position of the substituting groups on the specific volume of the solution is also considered in a few cases.

C. F. B.

**Action of Magnesium on Nitrogenous Compounds, especially Cyanides.** By W. EIDMANN (*J. pr. Chem.*, 1899, [ii], 59, 1—22).—When silicon nitride is heated with excess of magnesium powder in the absence of air, magnesium nitride and silicon, or magnesium silicide, are formed, as the residue yields ammonia when treated with water, and hydrogen and silicon hydride when treated with hydrochloric acid. With boron nitride, analogous results are obtained. With cyanogen, with hydrogen, methylic, ethylic, and phenylic cyanides, and with aniline, acetanilide, nitrobenzene, pyridine, quinoline, and carbazole, magnesium nitride and carbon are obtained, magnesium carbide also being produced in the case of compounds containing a cyanogen group.

The action on metallic cyanides was studied in greater detail in the case of barium cyanide. Coarse magnesium powder (about 3 at.) was mixed with this substance (1 mol.), the mixture placed in a nickel crucible, of which it occupied about one-third. covered with

asbestos paper, then with a thick layer of asbestos, and last of all with sand; the mixture was then heated with a small flame until a reaction occurred. The product yielded ammonia and acetylene when treated with water, and when crystallised barium cyanide had been used, a little hydrogen also; the aqueous solution contained barium hydroxide and undecomposed barium cyanide, and the residue consisted of magnesium hydroxide and unaltered magnesium. The original product must, therefore, have contained magnesium nitride, barium carbide, and barium; the last substance could, indeed, be separated by digesting the mass with mercury and pressing the amalgam formed through leather. Estimations of the amounts of ammonia and acetylene formed, showed that magnesium nitride is always produced in almost theoretical quantity, whilst the yield of carbide is below the theoretical, becoming less the higher the temperature to which the mixture is heated. This is explained by supposing that the main reaction takes place thus:  $\text{Ba}(\text{CN})_2 + 3\text{Mg} = \text{BaC}_2 + \text{Mg}_3\text{N}_2$ ; but that at the high temperature produced, some of the barium cyanide is decomposed thus:  $\text{Ba}(\text{CN})_2 = \text{Ba} + \text{C}_2\text{N}_2$ , the cyanogen being decomposed by the magnesium,  $\text{C}_2\text{N}_2 + 3\text{Mg} = \text{Mg}_3\text{N}_2 + 2\text{C}$ , so that the yield of cyanide is maintained at the theoretical. Variation of the proportion between the barium cyanide and the magnesium hardly seemed to influence the course of the reaction.

The action of magnesium on the cyanides examined is thus summarised. The reaction is more violent the more easily the cyanide is decomposed by heat; in addition to this decomposition, the reaction indicated in the first equation given above occurs to some extent, but if the carbide formed is easily decomposed by heat, as is the case with the carbides of the alkali metals and magnesium, it yields metal and carbon,  $\text{M}''\text{C}_2 = \text{M}'' + 2\text{C}$ . "The cyanides fall into three groups, as regards the action of magnesium on them. (1) Those which are stable at a red heat,  $\text{Ba}(\text{CN})_2$ ,  $\text{Ca}(\text{CN})_2$ ,  $\text{Sr}(\text{CN})_2$ ,  $\text{Mg}(\text{CN})_2$ ,  $\text{KCN}$ , and  $\text{NaCN}$ , react as soon as a red heat is reached and with no, or but a very mild, explosion, the temperature rising to a bright red heat. The product consists chiefly of magnesium nitride and metallic carbide. (2) Those cyanides which decompose at a red heat,  $\text{Zn}(\text{CN})_2$ ,  $\text{Cd}(\text{CN})_2$ ,  $\text{Ni}(\text{CN})_2$ ,  $\text{Co}(\text{CN})_2$ ,  $\text{Pb}(\text{CN})_2$ , and  $\text{Cu}_2(\text{CN})_2$ , are decomposed, with the production of a bright red heat and a feeble explosion. The residue consists chiefly of magnesium nitride, metal, and carbon. (3) Those cyanides which decompose below a red heat,  $\text{AgCN}$  and  $\text{Hg}(\text{CN})_2$ , first decompose, for the most part, into metal and cyanogen, on the latter of which the magnesium then acts with a violent explosion, a red heat being produced. The residue contains metal, carbon, and magnesium nitride, the last two of which must be regarded as resulting from the action of the magnesium on the cyanogen liberated."

C. F. B.

**Cyanide of Mercury.** By L. PRUSSIA (*Gazzetta*, 1898, 28, ii, 113—122).—Mercuric cyanide readily combines with other compounds of mercury, forming double salts.

A compound,  $\text{HgCl}_2 \cdot \text{HgCy}_2$ , is formed on dissolving the constituent salts in a small volume of water at 40—50°; the liquid deposits



microscopic octahedra and prisms, apparently dimetric, which are very soluble in water, and slightly so in boiling alcohol.

The compound  $\text{HgBr}_2 \cdot \text{HgCy}_2$  is produced on extracting with boiling alcohol an intimate mixture of mercuric bromide and cyanide in molecular proportion, and by slow evaporation of the solution is obtained in colourless, transparent prisms, which are very slightly soluble even in boiling water, and remain unchanged on exposure to the air.

The compound  $\text{Hg}(\text{NO}_3)_2 \cdot \text{HgCy}_2$  is formed when the constituent salts are ground up with a little water; it is a white, crystalline powder, very soluble in water, from which it crystallises in rhombic laminae. It readily decomposes on heating, even its hot aqueous solution evolving carbonic anhydride and depositing metallic mercury. Ethylic alcohol seems to decompose it, but a methylic alcohol solution is not affected even on boiling. Potassium hydroxide or sodium carbonate decomposes the aqueous solution.

By triturating together mercuric cyanide and acetate, a limpid liquid is obtained, which, after a short time, deposits a double salt of the composition  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{HgCy}_2$  in transparent, colourless prisms very soluble in water or alcohol. On adding caustic soda to its aqueous solution, crystalline mercuric oxycyanide is precipitated.

Mercuric cyanide differs in behaviour from most other metallic salts, as, for instance, in its stability towards alkali hydroxides; this points to the fact that its aqueous solution does not contain the ion  $\text{Hg}$ . Cryoscopic determinations in aqueous solutions show further that mercuric cyanide is not an electrolyte.

On adding caustic alkali to mercuric cyanide, slight decomposition sometimes occurs, so that on the addition of ferrous sulphate and a dilute acid, Prussian blue is precipitated; this is due, the author points out, to the presence in the alkali of small quantities of halogen salts which react with the mercuric cyanide, giving alkali cyanide and mercuric haloid.

The use of Plugge's reaction, namely, the evolution of hydrogen cyanide when mercuric cyanide is treated with common salt and oxalic acid, has been suggested for the toxicological estimation of mercuric cyanide. The author has devised an improved method of carrying out this process; he substitutes tartaric for oxalic acid, and uses a stream of carbonic anhydride to expel the hydrogen cyanide, which is absorbed by slightly ammoniacal silver nitrate: the addition of an acid to the solution precipitates silver cyanide, which can be weighed. By employing potassium bromide or iodide in place of common salt, the reaction is accelerated, and more accurate results are obtained.

T. H. P.

**Chromium Tetroxide Potassium Cyanide.** By O. FRITZ WIEDE (*Ber.*, 1899, 32, 378—387).—When the compound  $\text{CrO}_4 \cdot 3\text{NH}_3$ , prepared by the action of strong ammonia on perchromic acid (*Abstr.*, 1898, ii, 20), is treated with an aqueous solution of potassium cyanide, it dissolves with an intense, brownish-red coloration, ammonia being at the same time eliminated, and on adding alcohol, a brownish-red oil separates which solidifies in large crystals after some time.

*Chromium tetroxide potassium cyanide*,  $\text{CrO}_4 \cdot 3\text{KCN}$ , is readily soluble in water but insoluble in all other solvents; the brownish-red, aqueous solution gradually decomposes with elimination of hydrogen cyanide and formation of the chromate. Many salts produce characteristic precipitates; with dilute sulphuric acid, on warming, it is decomposed into hydrogen, oxygen, and chromic sulphate, but in the cold only a change of colour from brownish-red to violet occurs; this colouring matter may be extracted by means of ether, and is evidently due to chromium tetroxide hydrogen cyanide, which, however, cannot be isolated, the ethereal solution, on evaporation, yielding only chromate and hydrogen cyanide.

The potassium cyanide compound cannot be formed directly by adding an aqueous solution of potassium cyanide in alcohol to an ethereal solution of perchromic acid, as under these conditions a dark violet liquid separates, which when left solidifies, forming black crystals of the compound  $\text{KCrO}_5 + \text{H}_2\text{O}_2$ ; this is identical with the potassium salt of perchromic acid, previously described, but being in a much purer form has not only a darker colour, but is also crystalline and non-explosive; it cannot be obtained without hydrogen peroxide of crystallisation.

The paper concludes with measurements of the crystals both of chromium tetroxide ammonia and of chromium tetroxide potassium cyanide.

J. F. T.

**Barium Platinocyanide and Platinum free from Iridium.** By PAUL BERGSÖE (*Zeit. anorg. Chem.*, 1899, 19, 318—326).—Barium platinocyanide is best prepared by adding to a solution of hydrogen platinochloride the theoretical quantity of barium hydroxide and hydrogen cyanide, and treating the warm mixture with sulphurous anhydride until it becomes colourless; after removing the precipitated barium sulphate by filtration, the barium platinocyanide crystallises completely from the solution, as it is almost insoluble in a cold solution of barium chloride. The reaction which takes place in the preceding method is expressed by the equation  $\text{H}_2\text{PtCl}_6 + 4\text{HCN} + 5\text{Ba}(\text{OH})_2 + \text{SO}_2 = \text{BaPt}(\text{CN})_4 + 3\text{BaCl}_2 + \text{BaSO}_4 + 8\text{H}_2\text{O}$ .

The formation of barium platinocyanide proved to be a very convenient method for the preparation of platinum free from iridium, as this salt is easily purified by crystallisation from water, being soluble in 3—4 parts of boiling water and in 30 parts of cold water. Forty grams of platinum containing traces of iridium were mixed with a further 0.25 gram of iridium and converted into the barium double cyanide as described above. The barium platinocyanide was recrystallised three times from water, and the mother liquors evaporated to about one-third or one-fourth their volume, the further separations being mixed with the main product. The yield obtained was 30 grams, or 75 per cent., of platinum free from iridium; the barium sulphate precipitate contained 2.45 grams of platinum and 0.05 gram of iridium; the mother liquors contained 7.015 grams of platinum and 0.281 gram of iridium. This method gives a much better yield than that based on the purification by means of sodium platinochloride. Traces of osmium, ruthenium, and rhodium are completely removed with the iridium, but palladium, which forms a double cyanide isomorphous with

that of platinum, cannot be removed by this method; fortunately, however, it is easily and completely removed by the ordinary methods of purification.

The estimation of iridium in platinum when the iridium is present to the extent of 0.1 per cent. or above, is very quickly effected by comparing the colour of the precipitate obtained by adding potassium chloride with that of the precipitate obtained from a sample containing a known quantity of iridium. It is, however, necessary that both precipitates should be formed under precisely the same conditions as regards concentration, temperature, and the quantity of potassium chloride solution. When less than 0.1 per cent. of iridium is present, it is estimated according to the method described by Deville and Stas. The sample is heated with pure lead at  $1000^{\circ}$  for about five hours in a porcelain crucible in a current of coal gas; the lead alloy is treated with nitric acid, and the insoluble residue extracted with aqua regia, whereby the platinum is dissolved and the iridium and ruthenium remain insoluble. To remove any silicates which may be formed by action on the porcelain crucible, the residue of iridium is washed with hydrofluoric acid and finally ignited, reduced in a current of coal gas, and weighed. E. C. R.

**Double Thiocyanates of Vanadium and the Alkalis.** By A. Croci (*Zeit. anorg. Chem.*, 1899, 19, 308—317).—*Potassium vanadium thiocyanate*,  $V(SCN)_3 \cdot 3KSCN + 4H_2O$ , is obtained by dissolving vanadic anhydride in sulphuric acid, treating the solution with sulphurous anhydride, and after driving off the excess of the gas by heating on the water-bath, reducing the solution with the electric current until it becomes green. The green solution is then precipitated with potassium hydroxide, the theoretical quantity of potassium thiocyanate added, and the solution evaporated on the water-bath; the product is then extracted with 95 per cent. alcohol in order to remove the potassium sulphate, and the solution evaporated to dryness. This operation is twice repeated, and, finally, the salt is crystallised from water; it forms bright red crystals, which gradually become anhydrous when allowed to remain in a vacuum over sulphuric acid, or when heated at  $100^{\circ}$ , decomposes at  $110^{\circ}$ , and on further heating yields a black mass of partially reduced vanadic acid. It is easily soluble in water and alcohol, sparingly so in ether. The aqueous solution gives a precipitate of vanadium hydroxide when treated with alkalis or with ammonium sulphide. It is not precipitated by salts of magnesium, zinc, cadmium, manganese, cobalt, or nickel, but with copper sulphate it gives a black precipitate, and with mercurous nitrate a grey precipitate; both precipitates turn white after a time. With silver nitrate, it yields a reddish-brown precipitate which changes to violet and grey, and is blackened when treated with ammonia. Both the chemical reactions and the results obtained by the cryoscopic determination of the molecular weight show that the substance is a double salt, whereas potassium chromium thiocyanate is the salt of a complex acid.

*Ammonium vanadium thiocyanate*,  $V(SCN)_3 \cdot 3NH_4SCN + 4H_2O$ , separates in dark green to black crystals, and closely resembles the potassium salt.

*Sodium vanadium thiocyanate*,  $V(SCN)_3 \cdot 3NaSCN + 12H_2O$ , crystallises in large, red tablets or leaflets, is extremely hygroscopic, melts in its water of crystallisation at  $68^\circ$ , and is similar in other respects to the preceding salts.

Sodium chromocyanate has been described by Roesler as crystallising with  $7H_2O$ ; the author has prepared it according to Roesler's method, and finds that it crystallises with  $12H_2O$ . All the vanadium thiocyanate salts, therefore, have a composition analogous to that of the chromium salts.

The author was unable to obtain nickel and barium double salts of vanadium thiocyanate. E. C. R.

**Nitro-alcohols.** By JOSEPH MAAS (*Rec. Trav. Chim.*, 1898, 17, 384—398).— $\beta\beta$ -Bromonitroethylic alcohol,  $NO_2 \cdot CHBr \cdot CH_2 \cdot OH$ , prepared by the condensation of bromonitromethane with formaldehyde under the influence of a little potassium carbonate, is a thick, yellowish liquid having a pungent odour, boils at  $147$ — $148^\circ$  under 45 mm. pressure, and is sparingly soluble in water, but dissolves in ether and alcohol. Its molecular weight in water is normal; its sp. gr. is  $2.084$  at  $10^\circ$ , and its refractive index at ordinary temperature is  $1.52952$ . The *nitrate* is a somewhat viscid, yellowish liquid of sp. gr. =  $2.438$  at  $11^\circ$ . The *acetate* is a colourless liquid of sp. gr. =  $1.958$  at  $11^\circ$ , and boils at  $138$ — $142^\circ$  under 50 mm. pressure.

When bromonitroethylic alcohol is heated with water at  $135$ — $140^\circ$ , the liquid is found to have strong reducing properties, and yields a crystalline sodium salt on neutralisation and agitation with sodium hydrogen sulphite.

$\beta\beta$ -Bromonitrotrimethylenic glycol,  $NO_2 \cdot CBr(CH_2 \cdot OH)_2$ , obtained by the action of formaldehyde (2 mols.) on bromonitromethane (1 mol.) or bromonitroethylic alcohol (2 mols.) in presence of potassium carbonate, forms beautiful, colourless, transparent crystals, which are more or less octahedral in form; it melts at  $106$ — $107^\circ$ , is sparingly soluble in water, but dissolves in alcohol and ether, and has the normal molecular weight in water.

$\beta\beta$ -Bromonitroisopropylic alcohol,  $NO_2 \cdot CHBr \cdot CHMe \cdot OH$ , obtained from bromonitromethane and acetaldehyde, is a colourless liquid, but becomes yellow on exposure to light, has a faint but acid odour and a pungent taste; it has a sp. gr. =  $1.899$  at  $10^\circ$ , boils at  $149$ — $150^\circ$  under 42 mm. pressure, and has the normal molecular weight in cold water, in which it is almost insoluble, but dissolves in alcohol and ether. The *nitrate* is a colourless, oily liquid insoluble in water, and has a sp. gr. =  $2.134$  at  $10^\circ$ . The *acetate* is a colourless, oily liquid having a faint odour of acetic acid, has a sp. gr. =  $1.820$  at  $11^\circ$ , and boils at  $139$ — $141^\circ$  under 48 mm. pressure.

$\beta\beta$ -Bromonitrobutylenic  $\alpha\gamma$ -glycol,  $OH \cdot CHMe \cdot CBr(NO_2) \cdot CH_2 \cdot OH$ , is the product of interaction of acetaldehyde and bromonitroethylic alcohol or of formaldehyde and bromonitropropylic alcohol. It forms beautiful, transparent, colourless crystals, is insoluble in water, and melts at  $94$ — $96^\circ$ .

Bromonitromethane condenses with piperidylcarbinol, yielding a colourless, crystalline substance melting at  $49$ — $51^\circ$ , which rapidly

undergoes alteration and becomes brown ; it was not obtained in condition suitable for analysis. A. L.

**Acetonechloroform.** By FRANK K. CAMERON and H. A. HOLLY (*Journ. Physical Chem.*, 1898, 2, 322—335. Compare Willgerodt, *Abstr.*, 1882, 492 ; 1883, 1079 ; 1885, 648 ; 1888, 810 ; 1889, 689 ; 1890, 959).—The authors have repeated the greater part of Willgerodt's work, and come to the conclusion that there is but one acetonechloroform, a white, crystalline solid, which is trichlorotrimethylcarbinol,  $\text{CCl}_3 \cdot \text{CMe}_2 \cdot \text{OH}$ . This substance is not a simple additive product, and cannot be resolved into its original constituents by any direct means. It forms no definite hydrate. The temperature of the quadruple point for solid, two solutions and vapour, in the system acetonechloroform | water is  $75.2^\circ$ . Its melting point is near, but above  $97^\circ$ , and in all probability a perfectly anhydrous substance has not yet been obtained. The system acetonechloroform and water seems to present the remarkable case of a solid solution and two liquid solutions. J. J. S.

**Action of Zinc Chloride on Amylic Alcohol.** By J. WALTHER (*J. pr. Chem.*, 1899, [ii], 59, 41—45).—This reaction may be supposed to take place in two stages, like that of sulphuric acid on alcohol ; the first stage would be expressed by the equation,  $\text{C}_5\text{H}_{11} \cdot \text{OH} + \text{ZnCl}_2 = \text{C}_5\text{H}_{11} \cdot \text{O} \cdot \text{ZnCl} + \text{HCl}$ . To test this supposition, anhydrous amylic alcohol (1 mol.) was warmed with dry zinc chloride (1 mol.) until amylenes began to come off ; the zinc chloride dissolved gradually, and at  $40^\circ$  an evolution of gas commenced. The mixture was cooled and extracted with ether ; by adding light petroleum to the ethereal extract, a compound was precipitated, and this was purified by repeated solution in ether and precipitation with light petroleum. It forms a yellowish-red syrup, and yields amylic alcohol and zinc oxychloride when treated with water ; and small quantities of amylic alcohol, amylenes, diamylenes, and aldehyde, together with a pasty residue left in the flask, when it is distilled under either ordinary or diminished pressure. C. F. B.

**Synthesis of Dimethylheptenol.** By PHILIPPE BARBIER (*Compt. rend.*, 1899, 128, 110—111).—The synthesis of 2 : 6-dimethyl-2-heptene-6-ol has been effected by the general method devised by Saytzeff, in which, however, magnesium was used instead of zinc, a modification which was found to be of considerable service in this and other syntheses. Methyl iodide (113 grams) is gradually added to a well-cooled mixture of natural methylheptenone (100 grams) with anhydrous ether (150 grams) and magnesium turnings (20 grams) ; the magnesium compound formed is decomposed by dilute sulphuric acid, and the liquid which separates is purified by fractional distillation under diminished pressure. The dimethylheptenol which is thus obtained is a colourless liquid boiling at  $79-80^\circ$ , and is identical in every respect with the product of the action of alcoholic potash on lemonol. N. L.

**Biochemical Oxidation of Propylenic Glycol.** By ANDRÉ KLING (*Compt. rend.*, 1899, 128, 244—246).—When propylenic glycol

is mixed with an infusion of beer yeast, sterilised, inoculated with a culture of the sorbose bacterium and kept at 30°, it is partially converted into pyruvic aldehyde or into the acetol,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OH}$ , described by Perkin, probably the latter, but the point was not definitely determined.

Purification of propylenic glycol by distillation is unsatisfactory, since increasing quantities of aldehydes are formed, and they exert an antiseptic action in experiments with organisms. The best results are obtained by mixing the commercial "pure" propylenic glycol with its own volume of water, agitating five or six times with small quantities of ether, and then allowing the aqueous solution to evaporate over calcium chloride; the residual glycol is quite free from aldehydes.

C. H. B.

**Action of Liquid Hydrogen Iodide on Ether.** By F. G. COTTRELL and ROY RAYONE ROGERS (*Amer. Chem. J.*, 1899, 21, 64—66. Compare Abstr., 1896, ii, 357).—A vigorous action occurs when ether is mixed with an excess of liquid hydrogen iodide; the product, after remaining for a week, consists of ethylic iodide and water, the amount of the former substance produced is 94 per cent. of the theoretical ( $\text{Et}_2\text{O} : 2\text{EtI}$ ).

G. T. M.

***d*- and *r*-Arabinose.** By OTTO RUFF (*Ber.*, 1899, 32, 550—560).—By employing hydrogen peroxide and basic ferric acetate as an oxidising agent, a 25 per cent. yield of pure *d*-arabinose may be obtained from calcium *d*-gluconate.

*d*-Arabinose and *l*-arabinose both melt at 158·5—159·5 (corr.) when recrystallised from alcohol; *r*-arabinose melts at 163·5—164·5° (corr.), and is much more soluble than either of its active constituents; its true racemic nature is further shown by a determination of its molecular weight by the freezing point method. *d*-Arabitol, formed by the reduction of *d*-arabinose, melts at 103° (corr.), and *r*-arabitol at 105—106° (corr.); *d*-arabonic acid, prepared by the oxidation of *d*-arabinose with nitric acid, is a colourless syrup which, on heating, passes into the lactone; this crystallises from acetone in colourless needles melting at 98—99° (corr.). Calcium *d*-arabonate is identical in form with the *l*-modification, but a mixture of the two does not form a true racemic compound, but merely is a mixture of the two active constituents. *r*-Arabonic lactone crystallises from acetone in large, prismatic needles melting at 115—116° (corr.), and is less soluble in acetone than its active isomerides. *d*-Trihydroxyglutaric acid crystallises from acetone in hexagonal prisms melting at 128° (corr.). *r*-Trihydroxyglutaric acid melts at 154·5° (corr.), and is very similar in its properties to Fischer's *i*-xylotrihydroxyglutaric acid. The affinity constant of *l*-trihydroxyglutaric acid is nearly twice as great as that of the *r*-acid, the former being 0·132, and the latter 0·069.

J. F. T.

**Properties of Soluble Starch, and a Simple Method for its Preparation.** By AUGUSTIN WRÓBLEWSKI (*Chem. Zeit.*, 1898, 22, 375—376).—Soluble starch is the first product formed in the hydrolysis of starch; it is characterised by its solubility, by passing through

a porcelain filter, by not reducing Fehling's solution, and by giving a blue coloration with iodine. The author thinks it may also be regarded as the highest dextrin, although it differs in several of its properties from the ordinary dextrins (compare Lintner, *Abstr.*, 1898, i, 460). For the preparation of soluble starch, the following method is recommended. Hoffmann's rice starch (20 grams) is rubbed in a mortar with cold water (100 c.c.) poured into a 2-litre flask, boiling 0.5 per cent. aqueous potassium hydroxide (1 litre) is added, and the mixture well shaken; after being boiled for 1.5—2 hours, the solution is filtered, neutralised with dilute acetic acid, and the soluble starch precipitated with 95 per cent. alcohol. The precipitate is filtered, washed with 50 per cent., with 95 per cent., and with absolute alcohol, then with ether, and finally dried in a vacuum. The amount of alcohol required to precipitate soluble starch from aqueous solutions depends on the amounts of salts present, and if these are not present, it is advisable to add small quantities of neutral salts, such as potassium acetate.

It is thought that Syniewski's product, obtained by the action of sodium peroxide on starch, is not soluble starch, but a product of oxidation (*Abstr.*, 1898, i, 61). J. J. S.

**$\gamma$ -Amido- $\alpha\beta$ -propylenic Glycol.** By K. CHIARI (*Monatsh.*, 1898, 19, 571—583).—*Acetoallylamide*,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NHAc}$ , is obtained on adding excess of acetic anhydride gradually to well-cooled allylamine, heating on the water-bath, and finally distilling off the excess of acetic anhydride. It is a fairly mobile liquid, having a faint odour of garlic, and is freely soluble in water, alcohol, and ether; it becomes viscid at  $-20^\circ$  and boils at  $118\text{--}119^\circ$  under 17 mm. pressure.

*Aceto- $\beta\gamma$ -dibromopropylamide*,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{NHAc}$ , which is formed when bromine is added to a cooled solution of acetoallylamide in carbon tetrachloride, separates during the addition as a viscid, gum-like mass; it crystallises from ethylic acetate in silvery leaflets melting at  $134^\circ$  (uncorr.), dissolves in warm carbon tetrachloride and chloroform, and readily in alcohol and water, but is insoluble in benzene, ether, and light petroleum; it is very hygroscopic, and readily loses hydrogen bromide; it appears to crystallise with  $\text{H}_2\text{O}$ .

**$\gamma$ -Amido- $\alpha\beta$ -propylenic glycol**,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ , prepared by boiling acetodibromopropylamide with water during 24 hours, is a very hygroscopic, viscid liquid, which decomposes when distilled; it dissolves readily in water and alcohol, but is insoluble in ethylic acetate, ether, and benzene; when decomposed with nitrous acid, it yields glycerol. Its salts are very hygroscopic, and their solutions give a white, flocculent precipitate with mercuric chloride. Gold chloride is rapidly reduced by the aqueous solution of the hydrochloride. The *platinochloride*,  $(\text{C}_3\text{H}_7\text{O}_2\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises in golden yellow, shining needles, dissolves with exceptional readiness in water and alcohol, and melts at  $185^\circ$  (uncorr.).

**$\gamma$ -Ethylamido- $\alpha\beta$ -propylenic glycol**,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NHEt}$ , obtained by the action of ethylic iodide on the amido-glycol, is a thick, colourless liquid which boils at  $141\text{--}142^\circ$  under 18 mm. pressure; it is very readily soluble in water and alcohol, but insoluble in

ether, benzene, ethylic acetate, and chloroform. It dissolves in acids with evolution of heat.  $\gamma$ -Ethylamido- $\alpha\beta$ -propylenic diacetate,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{NHEt}$ , obtained on warming the amido-glycol with acetic anhydride, is an odourless liquid boiling at  $189\text{--}190^\circ$  under 16 mm. pressure; it is miscible in all proportions with water and alcohol, but is only sparingly soluble in benzene, ether, and similar solvents.

When allylamine dibromide is treated with alcoholic potash, a substance having the composition  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}$  or  $\text{C}_6\text{H}_{11}\text{NO}_2$  is produced in small quantities. This is a pale yellow, oily liquid, having a slight odour of pyridine; it boils at  $112\text{--}113^\circ$  under 16 mm. pressure, and dissolves readily in water, alcohol, and benzene, but somewhat sparingly in ether. A. L.

**Triethylamine Oxide.** By ARTHUR LACHMAN (*Ber.*, 1899, 32, 27).—Contrary to Hantzsch's statement, (*Abstr.*, 1898, i, 623), this compound does exist, and can be distilled without decomposing; it boils at  $152\text{--}158^\circ$ . It was prepared from nitroethane and zinc ethyl.

C. F. B.

**Methylethylpropylisobutylammonium Base.** By WILHELM MARCKWALD and ALBERT (FREIHERR) VON DROSTE-HUELSHOFF (*Ber.*, 1899, 32, 560—564).—Theoretically, this base is of great interest since, by the action of moulds, Le Bel seems to have obtained an optically active substance from its chloride, the activity being due to the presence of an asymmetrical quinquivalent nitrogen atom in the molecule. The present paper deals with a repetition of the work with results which are not in accordance with those obtained by Le Bel.

Starting with commercial ethylamine, paratoluenesulphonethylamide was first prepared by means of paratoluenesulphonic chloride and sodium hydroxide; this, on treatment with alcoholic potassium hydroxide and isobutylic bromide, was converted into paratoluenesulphonethylisobutylamide, which, on decomposition with chlorosulphonic acid, yielded *ethylisobutylamine*, a mobile liquid boiling at  $98^\circ$ , the *nitroso*-compound of which boils at  $193^\circ$ ; the *chloride* forms stable, white crystals, and melts and decomposes at  $209^\circ$ , and the *platinochloride* melts at  $201^\circ$ .

On boiling with sodium methylic sulphate in aqueous solution, this base was further converted into *methylethylisobutylamine*, a liquid boiling at  $105^\circ$ ; its *chloride* is hygroscopic, its *platinochloride* melts at  $197^\circ$ , and its *aurochloride* at  $99^\circ$ . *Methylethylpropylisobutylammonium iodide*, prepared quantitatively by the addition of propylic iodide to this base, melts at  $196.5^\circ$ ; the *platinochloride* melts with decomposition at  $236^\circ$ , and the *aurochloride* at  $103^\circ$ .

All attempts to obtain an optically active substance from this compound were failures. The authors are further engaged in investigating the asymmetry of the quinquivalent nitrogen atom when combined with five different radicles. J. F. T.

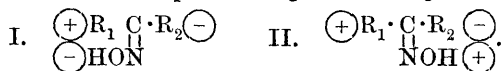
**Ethylideneimine.** By MARCEL DELÉPINE (*Compt. rend.*, 1899, 128, 105—108. Compare *Abstr.*, 1898, i, 462).—As the author has previously shown, aldehyde-ammonia may be regarded as the hydrate of ethylideneimine, which appears from the following considerations



to have the constitution  $\text{CHMe} \begin{smallmatrix} \text{NH} \cdot \text{CHMe} \\ \text{NH} \cdot \text{CHMe} \end{smallmatrix} \text{NH}$ . That aldehyde-ammonia is a hydrate is proved by its conversion into ethylideneimine when placed in a vacuum over sulphuric acid, and also by the fact, noticed by Liebig, that silver nitrate in aqueous solution yields with aldehyde-ammonia a salt of the formula  $(\text{C}_2\text{H}_5\text{N})_3 \cdot 1\frac{1}{2} \text{AgNO}_3$ , which contains no water. The formation of the substance  $\text{CHMe}(\text{NHBz})_2$ , which Limpricht obtained by the action of benzoic chloride on aldehyde-ammonia, indicates that a CHMe-group is united with two nitrogen atoms. From aldehyde-ammonia, Curtius has obtained nitrosoparalidine,  $\text{C}_6\text{H}_{12}\text{O}_2 \cdot \text{N} \cdot \text{NO}$ , the formation of which points to the existence of an imido-group, and the author has obtained the corresponding chlorine derivative by the action of sodium hypochlorite. *Chloroparalidine*,  $\text{CHMe} \begin{smallmatrix} \text{O} \cdot \text{CHMe} \\ \text{O} \cdot \text{CHMe} \end{smallmatrix} \text{NCl}$ , is an unstable oil, having a powerful odour, and is soluble in ether. In the presence of acetic acid, however, instead of this oil, a substance is obtained which crystallises in needles soluble in ether, and appears to have the composition  $\text{CHMe} \begin{smallmatrix} \text{NCl} \cdot \text{CHMe} \\ \text{NCl} \cdot \text{CHMe} \end{smallmatrix} \text{NCl}$ . A lower homologue of this substance, prepared in a similar manner and having the formula  $(\text{CH}_2 \cdot \text{NCl})_3$ , has been already described by the author. When an alcoholic solution of ethylideneimine is treated with hydrogen sulphide, it yields the theoretical quantity of thialdine, a compound which is also formed by the action of ammonia on thialdehyde, and is known to have the constitution  $\text{CHMe} \begin{smallmatrix} \text{S} \cdot \text{CHMe} \\ \text{S} \cdot \text{CHMe} \end{smallmatrix} \text{NH}$ . An intermediate compound, probably  $\text{CHMe} \begin{smallmatrix} \text{S} - \text{CHMe} \\ \text{NH} \cdot \text{CHMe} \end{smallmatrix} \text{NH}$ , was also obtained; it forms a crystalline hydrate melting at  $70^\circ$ , and is converted into thialdine by the further action of hydrogen sulphide.

It should be noted that in the majority of reactions, the tri-polymerised forms of aldehyde-ammonia and of ethylideneimine are involved, but that depolymerisation sometimes occurs. Such is the case when the compounds are volatilised or left in aqueous solution, and in certain chemical reactions as, for instance, the formation of carbothialdine,  $\text{CS}_2(\text{CHMe} \cdot \text{NH})_2$ . N. L.

**Stability of Stereoisomeric Oximes in Presence of Acids and Alkalis.** By RICHARD ABEGG (*Ber.*, 1899, 32, 291—297).—Whilst the oxime radicle acts as a base in acid or neutral solution, and therefore receives the + charge of a cation when dissociated electrolytically, it becomes the anion in an alkaline solution, and receives a - charge. The supposition is made, therefore, that the form I will be the more stable in alkaline solution, and the form II in acid solution, when the radicle  $\text{R}_1$  is electropositive compared with  $\text{R}_2$ .



Four examples are quoted in support of this theory. T. M. L.

**Action of Ethylenediamine on Isobutaldehyde, Isovaleraldehyde, Acetaldehyde, and Glyoxal.** By EDMUND KOLDA (*Monatsh.*, 1898, 17, 609—626).—Ethylenediamine readily reacts with isobutaldehyde, forming a condensation product,  $C_{10}H_{20}N_2$ , which is a thick, colourless liquid boiling at  $87-89^\circ$  under 18 mm. pressure, and has strongly basic properties. It is decomposed by boiling water, forming ethylenediamine and isobutaldehyde, and is also decomposed by bromine, yielding ethylenediamine hydrobromide. The *platinochloride* is an amorphous, yellow powder. The condensation product of isovaleraldehyde and ethylenediamine boils at  $123-125^\circ$  under 20 mm. pressure, and resembles the foregoing compound in its properties; the *platinochloride* is an amorphous, yellow powder. When ethylenediamine reacts with acetaldehyde, a portion of the latter is converted into aldol, which reacts with acetaldehyde and ethylenediamine in molecular proportion, forming a product,  $CHMe \cdot N \cdot C_2H_4 \cdot N \cdot CH \cdot CH_2 \cdot CHMe \cdot OH$ , which crystallises in large rhombohedra, melts at  $111-113^\circ$  and forms an amorphous, yellow *platinochloride*. When boiled with water, the condensation product decomposes, yielding ethylenediamine and a resinous mass, the odour of aldehyde and crotonaldehyde being noticed during the decomposition. Glyoxal reacts with ethylenediamine forming an amorphous mass which melts at  $145-146^\circ$ , and probably has the constitution  $CHO \cdot CH < \begin{matrix} NH \cdot C_2H_4 \cdot N \cdot CH \\ NH \cdot C_2H_4 \cdot N \cdot CH \end{matrix}$ . This substance is decomposed by boiling water, and yields a reddish-brown, amorphous *platinochloride*.

A. H.

**Action of Potassium Cyanide on Aliphatic Aldehydes.** By LEOPOLD KOHN (*Monatsh.*, 1898, 19, 519—523).—Potassium cyanide acts on many aliphatic aldehydes, producing condensation products of the aldol type; thus propaldehyde and valeraldehyde yield the corresponding aldols, whilst acetaldehyde suffers further change, and is converted into a substance of higher molecular weight.

When isobutaldehyde is treated with potassium cyanide, *isobutaldol cyanhydrin*,  $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CH(OH) \cdot CN$ , is produced; the formation of this substance is accounted for by the fact that isovaleric acid is a product of the reaction, and this liberates hydrogen cyanide, which attacks the isobutaldol formed, in the usual manner. The cyanhydrin crystallises in measurable, colourless tablets, and melts at  $140^\circ$ ; it is insoluble in water and ether, but dissolves in hot alcohol. When treated with potash, it yields isobutyric acid, potassium cyanide, and *octylic glycol*,  $CHMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CH_2 \cdot OH$ ; the last-named crystallises in tables and melts at  $51.5^\circ$ .

On hydrolysis, the cyanhydrin yields a crystalline *hydroxy-γ-lactone*,  $C_9H_{16}O_3$ , which dissolves readily in alcohol and ether, melts at  $92.5^\circ$ , and, on treatment with alkalis, yields salts of the corresponding dihydroxy-acid; the *acetate* forms measurable crystals, and melts at  $59^\circ$ . When oxidised by potassium permanganate, the hydroxylactone yields isobutyric acid and a ketonic acid, possibly isobutyrylformic acid, the formation of these substances being probably preceded

by that of the  $\alpha\gamma$ -diketonic acid,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CMe}_2 \cdot \text{CO} \cdot \text{COOH}$ , which would give these two products on hydrolysis. A. L.

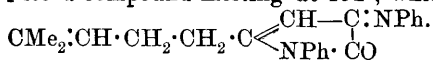
**Action of Hydrazine Hydrate on Isobutaldol.** By ADOLF FRANKE (*Monatsh.*, 1898, 19, 524—535).—Hydrazine hydrate, in 50 per cent. aqueous solution, reacts with pure isobutaldol at  $60^\circ$ , and the product may be separated by fractional distillation into two portions, boiling at  $163$ — $165^\circ$  and at  $230^\circ$  respectively. The former, which is *isobutaldazine*,  $\text{N}_2(\text{:CH} \cdot \text{CHMe}_2)_2$ , may also be obtained by the action of isobutaldehyde on hydrazine hydrate; it is a pale yellow oil having a penetrating odour. Its solution, in dilute hydrochloric acid, colours woody tissue an intense yellow, and, in this respect, it resembles pyrazoline derivatives, but it does not give Knorr's pyrazoline reaction. When the aldazine, dissolved in chloroform, is treated with bromine at  $-10^\circ$ , hydrogen bromide is evolved, but crystalline products could not be isolated. The *hydrochloride*,  $\text{C}_8\text{H}_{16}\text{N}_2 \cdot \text{HCl}$ , is readily soluble in water and alcohol, sparingly so in cold alcohol, and insoluble in ether; it forms beautiful crystals and melts at  $149^\circ$ ; its boiling aqueous solution has a distinct camphor-like odour. The *platinohydrochloride*,  $(\text{C}_8\text{H}_{16}\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$ , a sulphur-yellow, flocculent precipitate, melts and decomposes at  $146^\circ$ . The *argentonitrate*,  $\text{C}_8\text{H}_{16}\text{N}_2 \cdot \text{AgNO}_3$ , is obtained as a white, crystalline precipitate when silver nitrate is added to the aqueous solution of the aldazine; it is sparingly soluble in cold, but readily in hot water, and, on adding ammonia to the solution, metallic silver is precipitated.

When the hydrochloride is treated with dilute aqueous soda, a compound,  $\text{C}_8\text{H}_{16}\text{N}_2$ , isomeric with the aldazine, is obtained in quantitative amount; it is a colourless oil having the odour of camphor, and boils at  $192^\circ$ ; it does not form a crystalline hydrochloride or argentonitrate, and, when boiled with dilute sulphuric acid, does not yield isobutaldehyde and hydrazine, but gives products the investigation of which is being continued.

*Di-isobutylhydrazine*,  $\text{N}_2\text{H}_2(\text{CH}_2 \cdot \text{CHMe}_2)_2$ , obtained when isobutaldazine is reduced with sodium and alcohol, boils at  $170$ — $175^\circ$ , and has the odour and properties of an amine; the *hydrochloride*,  $\text{C}_8\text{H}_{20}\text{N}_2 \cdot 2\text{HCl}$ , melts and decomposes at  $175^\circ$ . Isobutylamine is also a product of the reduction of isobutylaldazine. A. L.

**Derivatives of Synthetic Methylheptenone.** By GEORGES LÉSER (*Compt. rend.*, 1899, 128, 108—110).—*Methylhexenonepyruvic acid*, or 8-methyl-7-nonene-2:4-dionoic acid, is readily obtained by the action of sodium ethoxide and ethylic oxalate on methylheptenone, and crystallises in fine, colourless prisms melting at  $39$ — $50^\circ$  (?), and very soluble in most organic solvents, with the exception of cold carbon bisulphide. It forms well-crystallised salts, from which the acid is not liberated by acetic acid; the silver salt crystallises in silky needles, which become coloured on exposure to light. When ethereal solutions of methylhexenonepyruvic acid (1. mol.) and of aniline (2 mols.) are mixed, a mass of crystals is obtained, probably of the aniline salt of the acid; this, however, cannot be isolated, as the crystals rapidly lose water and are converted into the aniline salt of the *phenylimide*,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}(\text{NPh}) \cdot \text{COONH}_3\text{Ph}$ . This sub-

stance melts at  $82^{\circ}$ , and at the same time loses  $2\text{H}_2\text{O}$ , and is converted into a compound melting at  $152^{\circ}$ , which probably has the constitution



The same compound is obtained by boiling a solution, in methylic alcohol, of the aniline salt of the phenylimide, and also by the direct action of aniline on methylhexenonepyruvic acid at  $100^{\circ}$ , or at the boiling point of aniline. In the cold, ammonia behaves towards methylhexenonepyruvic acid like aniline, yielding the ammonium salt of an imido-acid; but, on warming the solution, ammonia is evolved. This reaction will be further studied.

When heated at  $90$ — $100^{\circ}$ , methylhexenonepyruvic acid loses carbonic anhydride and is converted into *methyl-octenonal*,  $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHO}$ , which is more readily prepared by the action of ethylic formate on methylheptenone in presence of sodium ethoxide. This compound, the first  $\beta$ -ketonic aldehyde isolated, crystallises from alcohol in colourless, nacreous tablets, melting at  $73^{\circ}$ , and having an agreeable odour resembling that of citronellal. It yields, with cupric acetate, a salt,  $\text{Cu}(\text{C}_9\text{H}_{13}\text{O}_2)_2$ , which will be subsequently described. N. L.

**Action of Chlorine on Isobutylacetic Acid.** By CLEMENTE MONTEMARTINI (*Gazzetta*, 1898, 28, ii, 290—295).—The author finds that when isobutylacetic acid is chlorinated under the conditions employed in his previous work on the chlorination of isovaleric acid (Abstr., 1898, i, 236), the principal product is  $\gamma$ -chlorisobutylacetic acid; in this case, as also with isovaleric acid (*loc. cit.*) and isobutyric acid (Balbiano, Abstr., 1879, 615), the tertiary hydrogen atom is replaced, and from these results the author concludes that when chlorine acts, under the direct influence of the sun's rays and at a temperature of about  $100^{\circ}$ , on a monobasic acid containing the group  $\text{CHMe}_2$ , the hydrogen atom of the CH-group is always replaced, no matter what may be its distance from the carboxyl group. T. H. P.

**Oleodistearin, and the Iodine Number.** By ROBERT HENRIQUES and HERM. KÜNNE (*Ber.*, 1899, 32, 387—394).—Doubt having been cast on Heise's statement that the glyceride extracted from Mkani fat is oleodistearin (*Arbeit kaiserl. Gesundheitsamt*, 1896, 540), the authors have reinvestigated this substance, and find that Heise's view is correct.

Oleodistearin,  $\text{C}_3\text{H}_5(\text{C}_{18}\text{H}_{35}\text{O}_2)_2(\text{C}_{18}\text{H}_{33}\text{O}_2)$ , crystallises from a mixture of alcohol and ether in small, snow-white crystals melting at  $45$ — $46^{\circ}$  and having an iodine number of 28.8; when treated in ethereal solution with an alcoholic solution of iodine chloride, it yields a *chloriodo*-additive product melting at  $44.5$ — $45.5^{\circ}$ , and closely resembling oleodistearin, both in its behaviour towards solvents and in the fact that, when fused and resolidified, it melts  $3$ — $4^{\circ}$  lower than before. This additive product is remarkably stable both towards acid and alkali, and only on heating in sealed tubes at  $150^{\circ}$  with alcoholic ammonia are the halogens completely eliminated and the glyceride reformed.

Like oleic acid, oleodistearin can undergo the elaidin rearrangement, although it does not do so as readily. When the red nitrous fumes from a mixture of nitrite and sulphuric acid are conducted into the melted glyceride, crystals of *elaidodistearin* are formed; this, after recrystallisation from a mixture of alcohol and ether, melts at  $61^{\circ}$  and closely resembles oleodistearin, but is less soluble in the ordinary solvents; with an alcoholic solution of iodine chloride, it forms a *chlorido*-compound which separates from a mixture of alcohol and ether in crystals melting at  $57-58^{\circ}$ . J. F. T.

**Two Modifications of Ethylic  $\beta$ -Aminocrotonate.** By ROBERT BEHREND (*Ber.*, 1899, 32, 544—546).—There are two modifications of ethylic  $\beta$ -aminocrotonate, melting at  $20^{\circ}$  and at  $33^{\circ}$  respectively; the former is produced when ethylic acetoacetate is treated with gaseous ammonia at  $60^{\circ}$ , the latter when a cooled ethereal solution of the ethylic salt is saturated with ammonia in the presence of ammonium nitrate. The conversion of one form into the other can be effected as often as required, since, on crystallising at temperatures below  $19^{\circ}$ , the form of lower melting point separates, whilst in contact with a crystal of the form of higher melting point the other modification separates. Further, on touching the crystals melting at  $20^{\circ}$  with the form of higher melting point, they are converted into the latter with development of heat. J. F. T.

**Condensation of the Fatty Aldehydes with Propionic Acid.** By FRANZ KIETREIBER (*Monatsh.*, 1898, 19, 727—737).—Isobutaldehyde, sodium propionate, and propionic anhydride react at  $190-200^{\circ}$ , forming *methylisobutylideneacetic acid*,  $\text{CHMe}_2\cdot\text{CH}:\text{CMe}\cdot\text{COOH}$ , in small amount; it is a colourless, oily liquid which boils at  $115-116^{\circ}$  under 15 mm. pressure. The *calcium* salt crystallises in silky needles, whilst the *silver* salt is a crystalline precipitate. With bromine, the acid yields a *dibromide*; this forms yellowish-white crystals, melts at  $73^{\circ}$ , and is converted by alkalis into the corresponding *dihydroxy*-acid, which crystallises in white plates melting at  $114-115^{\circ}$ . Acetaldehyde reacts with sodium propionate and propionic anhydride in the normal manner, tiglic acid,  $\text{CHMe}:\text{CMe}\cdot\text{COOH}$ , being produced, but with  $\alpha$ -nthaldehyde there was no reaction.

A. H.

**Chlorides of Monethylic Salts of Dibasic Acids.** By EDMOND E. BLAISE (*Compt. rend.*, 1899, 128, 183—185).—When the chloride of a monethylic salt of a dibasic acid,  $\text{COCl}\cdot\text{R}''\cdot\text{COOEt}$ , is distilled, it partially decomposes into the normal alkylic salt and the dichloride of the acid, together with some anhydride and ethylic chloride, these reactions being also reversible. The author has therefore endeavoured to prepare these chlorides at a low temperature. When sodium ethoxide is added gradually to an alcoholic solution of the anhydride of the acid, cooled in ice, the product consists entirely of the sodium alkylic salt. The alkylic hydrogen salt is separated by acidifying the aqueous solution of the sodium alkylic salt, and after being dried over sulphuric acid is heated at about  $60^{\circ}$  for an hour with the calculated quantity of phosphorus trichloride. The monochloride thus obtained

is treated directly with zinc methyl. In this way, dimethyllevulinic acid,  $\text{COMe} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , and dimethylhexanonic acid,  $\text{COMe} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , have been prepared identical with those obtained by the oxidation of campholene and  $\beta$ -campholenic acid respectively.

C. H. B.

**Isobutylsuccinic Acid.** By EDVARD HJELT (*Ber.*, 1899, 32, 529).—Isobutylsuccinic acid (Fittig and Burwell, Fittig and Thron, this vol., i, 336 and 337), when crystallised from benzene, melts at  $105^\circ$ , but at  $107^\circ$  when crystallised from water. The *paratolilic acid* and *paratolil* of isobutylsuccinic acid melt at  $135$ — $136^\circ$  and  $104$ — $108^\circ$  respectively.

M. O. F.

**Transformation of Unsaturated Acids.** By RUDOLPH FITTIG (*Annalen*, 1899, 304, 117—145).—The paper summarises the experimental results described in the following abstracts.

M. O. F.

**Itaconic, Citraconic, and Mesaconic Acids.**—By RUDOLPH FITTIG and CHARLES FORD LANGWORTHY (*Annalen*, 1899, 304, 145—156. Compare Abstr., 1893, i, 189).—Contrary to the statement of Franz (*Abstr.*, 1894, i, 404), itaconic acid does not pass over in a current of steam, and hence may be separated with mesaconic acid from the isomeric citraconic acid which is volatile in steam. The barium salt contains  $\frac{1}{2}\text{H}_2\text{O}$ ; 100 parts of the aqueous solution saturated at  $20^\circ$  contain 7.61 parts of the anhydrous salt.

Citraconic acid crystallises in thin, flattened needles when petroleum is added to its solution in ether; it melts and decomposes at  $91^\circ$ . In the purified state, it undergoes no change in the desiccator, but when impure it becomes transformed into itaconic acid. The barium salt contains  $2\frac{1}{2}\text{H}_2\text{O}$ ; 100 parts of the aqueous solution saturated at  $12^\circ$  contain 0.29 part of the anhydrous salt.

Barium mesaconate contains  $4\text{H}_2\text{O}$ ; 100 parts of the aqueous solution saturated at  $15.5^\circ$  contain 4.6 parts of the anhydrous salt.

When a 25 per cent. solution of bromine in chloroform is added to citraconic acid dissolved in a mixture of ether and chloroform, and the liquid exposed to sunlight, mesaconic acid is quickly precipitated; the transformation takes place more slowly under the influence of diffused light, or when aqueous solutions are employed, and does not take place at all in the dark. The analogous transformation of maleic into fumaric acid has been ascribed by Wislicenus to the addition and removal of hydrogen bromide arising from secondary reactions; this explanation does not apply in the present instance, however, because hydrogen bromide has no influence on citraconic acid dissolved in a mixture of ether and chloroform, even when exposed to direct sunlight.

The action of a boiling 10 per cent. solution of caustic soda converts itaconic acid into mesaconic acid to the extent of about 80 per cent.; this action is reversible, nearly 20 per cent. of itaconic acid being obtainable from mesaconic acid. By the same agency, citraconic acid is converted into mesaconic and itaconic acid, in quantities amounting to 60 per cent. and 20 per cent. respectively.

When itaconic acid is reduced, in acid solution, with sodium amalgam, it is converted into pyrotartaric acid to the extent of about 94 per cent. M. O. F.

**Pyrocinchonic Acid and its Isomerides.** By RUDOLPH FITTIG and ARTHUR KETTNER (*Annalen*, 1899, 304, 156—178. Compare Abstr., 1896, i, 599).—Experimental details of the conversion of pyrocinchonic (dimethylmaleic) acid into  $\beta$ -methylmesaconic and  $\beta$ -methylitaconic acids are described in this paper (compare *loc. cit.*).

The *silver* salt of dimethylfumaric ( $\beta$ -methylmesaconic) acid is crystalline, the *calcium* salt contains  $2\text{H}_2\text{O}$ , and the barium salt  $2\frac{1}{2}\text{H}_2\text{O}$ . When dimethylfumaric acid is distilled, it is, in part, converted into pyrocinchonic anhydride, which is also formed on treating the acid with acetic chloride.

The *silver* salt of methylitaconic acid is scarcely soluble in water; the *calcium* salt is crystalline, and contains  $1\text{H}_2\text{O}$ . Distillation converts the acid into pyrocinchonic anhydride, but hot acetic chloride gives rise to methylitaconic *anhydride*,  $\text{C}_6\text{H}_6\text{O}_3$ , which crystallises from carbon bisulphide in small, lustrous leaflets and melts at  $62\text{--}63^\circ$ ; when distilled, the anhydride yields pyrocinchonic anhydride, and warm water converts it into methylitaconic acid.

Although bromine converts citraconic acid into mesaconic acid (preceding abstract), dimethylfumaric acid is transformed by the halogen, under the same conditions, into pyrocinchonic anhydride, the anhydride of dimethylmaleic acid. Methylitaconic acid, on the other hand, gives rise to the *dibromide*,  $\text{C}_6\text{H}_8\text{Br}_2\text{O}_4$ , which crystallises from ether, and melts at  $153^\circ$ , when it decomposes.

A boiling solution of caustic soda leaves dimethylfumaric acid, for the most part, unchanged; methylitaconic acid, however, yields 50 per cent. of pyrocinchonic anhydride, and 28 per cent. of dimethylfumaric acid. Towards nascent hydrogen, furnished by sodium amalgam in feebly alkaline solution, dimethylfumaric and methylitaconic acids behave alike; both yield a mixture of *cis*- and *trans*-dimethylsuccinic acids. M. O. F.

**Ethylitaconic Acid and its Isomerides.** By RUDOLPH FITTIG and FRITZ GLASER (*Annalen*, 1899, 304, 178—194. Compare Abstr., 1893, i, 189).—The *ethyllic* salt of ethylparaconic acid boils at  $278\text{--}279^\circ$ , and does not solidify at  $-18^\circ$ ; it is converted into ethylitaconic acid under the influence of sodium ethoxide.

*Ethylitaconic acid*,  $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$ , which melts and decomposes at  $162\text{--}167^\circ$ , is readily soluble in hot water, but requires 74 parts of cold water to dissolve it. The *barium* salt contains  $2\text{H}_2\text{O}$ , and the *calcium* salt  $1\text{H}_2\text{O}$ , the *silver* salt being anhydrous.

*Ethylcitraconic acid*,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}(\text{COOH})\cdot\text{CH}\cdot\text{COOH}$ , crystallises from petroleum in aggregates of needles and melts at  $93\text{--}95^\circ$ , forming the anhydride. The *barium* salt contains  $\frac{1}{2}\text{H}_2\text{O}$ , and the *calcium* salt  $1\text{H}_2\text{O}$ , whilst the *silver* salt is anhydrous. The *anhydride*, produced when ethylitaconic acid is submitted to dry distillation, is a yellow oil which boils at  $240\text{--}245^\circ$ . When aqueous ethylcitraconic acid is boiled during 2 hours in a reflux apparatus, it is, in part, converted into ethylitaconic acid.

*Ethylmesaconic acid*,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}(\text{COOH})\cdot\text{CH}\cdot\text{COOH}$ , is obtained from ethylcitraconic acid under the influence of nitric acid, or by the action of bromine in direct sunlight; it melts at  $174\text{--}175^\circ$ , and dissolves in 90 parts of cold water. The *barium* and *silver* salts are anhydrous, and crystallise in needles.

The three foregoing acids are converted into propylsuccinic acid by the action of sodium amalgam.

*Ethylitadibromopyrotartaric acid*,  $\text{C}_7\text{H}_{10}\text{Br}_2\text{O}_4$ , prepared by the action of bromine dissolved in chloroform on ethylitaconic acid, melts and decomposes at  $153\text{--}154^\circ$ . When the viscous mother liquor is boiled with water and distilled, two acids are obtained; the non-volatile substance is probably *ethaconic acid*,  $\text{C}_7\text{H}_8\text{O}_4$ , melting at  $145\text{--}146^\circ$ . *Bromohexenoic* ( $\beta$ -*bromohydrosorbic*) *acid*,  $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{COOH}$ , distils in an atmosphere of steam, and is formed by the elimination of the elements of carbonic anhydride and hydrogen bromide from ethylitadibromopyrotartaric acid; it crystallises from water in nacreous leaflets, melts at  $51\text{--}52^\circ$ , and on reduction with sodium amalgam, yields hydrosorbic acid.

*Ethylitabromopyrotartaric acid*,  $\text{C}_7\text{H}_{11}\text{BrO}_4$ , obtained by the action of hydrogen bromide on ethylitaconic acid, crystallises from water in small prisms and melts at  $145\text{--}146^\circ$ , losing hydrogen bromide; boiling water converts it into ethylparaconic acid.

*Ethylcitrabromopyrotartaric acid*,  $\text{C}_7\text{H}_{11}\text{BrO}_4$ , prepared by the action of hydrogen bromide on ethylcitraconic acid, melts at  $119\text{--}121^\circ$ ; it is distinguished from its isomeride by the high degree of solubility in water and in warm chloroform.

M. O. F.

**Dimethylitaconic (Teraconic) Acid and its Isomerides.** By RUDOLPH FITTIG and HERMANN KRAFFT (*Annalen*, 1899, 304, 195—207).—Teraconic acid is obtained by the action of sodium ethoxide on the ethylic salt of terebic acid. The *anhydride*, produced on heating the acid at  $200^\circ$ , crystallises from carbon bisulphide in lustrous leaflets; it melts at  $44^\circ$  and boils at  $197^\circ$  and  $275\text{--}283^\circ$  under pressures of 22 mm. and 760 mm. respectively.

*Dimethylcitraconic acid*,  $\text{CHMe}_2\cdot\text{C}(\text{COOH})\cdot\text{CH}\cdot\text{COOH}$ , crystallises from petroleum in aggregates of needles and melts at  $91\text{--}93^\circ$ , when it decomposes; the *barium* salt contains  $1\frac{1}{2}\text{H}_2\text{O}$ , and the *calcium* salt  $1\text{H}_2\text{O}$ , the *silver* salt being anhydrous. The *anhydride* is produced with teraconic anhydride when teraconic acid is distilled under atmospheric pressure.

*Dimethylmesaconic acid*,  $\text{CHMe}_2\cdot\text{C}(\text{COOH})\cdot\text{CH}\cdot\text{COOH}$ , prepared by the action of bromine in chloroform on dimethylcitraconic acid, crystallises from water and melts at  $185^\circ$ ; it is identical with Demarcay's iso-oxyhexic acid, prepared from ethylic isopropylacetate by Walden's method. The *barium* salt contains  $4\text{H}_2\text{O}$ , and the *calcium* salt  $2\text{H}_2\text{O}$ ; the *silver* salt crystallises from boiling water in aggregates of small needles. When dimethylmesaconic acid is submitted to dry distillation, it yields 21 per cent. of dimethylcitraconic acid and 12 per cent. of teraconic acid; dimethylcitraconic acid is also converted into teraconic acid when heated with water in sealed tubes at  $150\text{--}160^\circ$ . The foregoing acids are comparatively indifferent



towards boiling aqueous alkalis; sodium amalgam reduces them to isopropylsuccinic acid. M. O. F.

**Dimethylaticonic Acid.** By RUDOLPH FITTIG and NICOLAUS PETKOW (*Annalen*, 1899, 304, 208—240).—*Dimethylaticonic acid*,  $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$ , prepared by the action of a boiling 20 per cent. solution of caustic soda on teraconic acid, is separated from the latter with considerable difficulty; it separates from water in aggregates of small crystals, and melts at  $146\text{--}147^\circ$ . The acid dissolves more readily than teraconic acid in water and in ether, 100 parts of the former solvent at  $15^\circ$  dissolving 1.49 parts of teraconic acid and 7.56 parts of dimethylaticonic acid; 100 parts of ether at  $15^\circ$  dissolve 1.37 parts and 19.47 parts of the respective acids. The *calcium* salt contains  $2\text{H}_2\text{O}$ , and the *barium* salt  $1\text{H}_2\text{O}$ ; the *anhydride*, obtained by distilling the acid at  $170\text{--}200^\circ$  under 20 mm. pressure, remains viscous at  $-20^\circ$ . Boiling water resolves dimethylaticonic acid into isocapro lactone, terebic acid, and a small proportion of teraconic acid; boiling dilute sulphuric acid converts it into terebic acid, whilst a boiling 20 per cent. solution of caustic soda regenerates teraconic acid.

*Bromisoterebic acid*,  $\text{C}_7\text{H}_9\text{BrO}_4$ , obtained by the action of bromine in chloroform on dimethylaticonic acid, melts at  $130\text{--}131^\circ$ , and separates from water in large, lustrous crystals belonging to the rhombic system:  $a:b:c=0.9702:1:0.7846$ . *Isoheptodilactone*,  $\text{C}_7\text{H}_8\text{O}_4$ , prepared from bromisoterebic acid by the action of alkalis, melts at  $115^\circ$ , and is converted by alkalis into the salts of a dibasic dihydroxy-acid; the *barium* salt contains  $1\text{H}_2\text{O}$ , and the *calcium* salt  $1\frac{1}{2}\text{H}_2\text{O}$ , whilst the *silver* salt is anhydrous. *Hydroxyisoterebic acid*,  $\text{C}_7\text{H}_{10}\text{O}_5$ , another product of the action of alkalis on bromisoterebic acid, melts at  $163^\circ$ , and is identical with the compound obtained by Roser from chloroterebic acid; it separates from water in highly lustrous crystals belonging to the monoclinic system:  $a:b:c=0.8870:1:0.8241$ ;  $\beta=88^\circ 29' 35''$ . The *barium* salt contains  $1\text{H}_2\text{O}$ , and the *calcium* salt  $\frac{1}{2}\text{H}_2\text{O}$ ; the *silver* salt separates from water in small, colourless crystals. Prolonged treatment with concentrated boiling alkalis resolves hydroxyisoterebic acid into the salts of the dibasic acid derived by the same method from isoheptodilactone.

*Isoterebilenic acid*,  $\text{C}_7\text{H}_8\text{O}_4$ , is obtained by boiling an aqueous solution of isoheptodilactone during 10 hours, evaporating the solution, and removing the unchanged lactone which separates; it is also produced in small amount when hydroxyisoterebic acid is heated with fuming hydrogen bromide in sealed tubes at  $100\text{--}120^\circ$ . It melts at  $118\text{--}119^\circ$ , and forms large crystals belonging to the monoclinic system:  $a:b:c=1.147:1:1.510$ ;  $\beta=78^\circ 57'$ . The *barium* salt contains  $1\text{H}_2\text{O}$ , and the *calcium* salt  $\frac{1}{2}\text{H}_2\text{O}$ ; the *silver* salt separates from water in well-formed crystals.

*Isoterebic (dimethylisoparaconic) acid*,  $\text{C}_7\text{H}_{10}\text{O}_4$ , prepared by reducing isoterebilenic acid with sodium amalgam, is insoluble in petroleum and melts at  $77\text{--}78^\circ$ ; the *calcium* salt contains  $1\text{H}_2\text{O}$ , and the *barium* and *silver* salts are anhydrous. Isoterebic acid is resolved by barium

hydroxide into a salt of the acid  $C_7H_{12}O_5$ , corresponding with diaterebic acid; the *barium* and *silver* salts are anhydrous. M. O. F.

**Propylitaconic Acid and its Isomerides.** By RUDOLPH FITTIG and FRITZ FICHTER (*Annalen*, 1899, 304, 241—258).—Propylitaconic acid,  $CHPr^{\alpha}:C(COOH):CH_2\cdot COOH$  (compare Abstr., 1890, 589), prepared by the action of sodium ethoxide on ethylic propylparaconate, melts and decomposes at  $159-160.5^{\circ}$ ; the *calcium* salt contains  $1H_2O$ , and the *barium* salt is anhydrous. When the acid is heated with fuming hydrochloric acid in a sealed tube at  $120^{\circ}$ , propylparaconic acid is regenerated.

*Propylcitraconic acid*,  $CH_2Pr^{\alpha}:C(COOH):CH\cdot COOH$ , obtained on distilling propylitaconic acid, crystallises from a mixture of ether and petroleum in transparent plates and melts at  $80^{\circ}$ , forming the anhydride; the *calcium* salt contains  $1H_2O$ , whilst the *barium* and *silver* salts are anhydrous. When heated with water in a sealed tube at  $160^{\circ}$ , propylcitraconic acid is converted into propylitaconic acid.

*Propylmesaconic acid*,  $CH_2Pr^{\alpha}:C(COOH):CH\cdot COOH$ , produced on treating propylcitraconic acid in chloroform with a solution of bromine in the same medium, crystallises from water in slender needles and melts at  $170^{\circ}$ ; it boils at  $240^{\circ}$  under a pressure of 16 mm. The *calcium* salt contains  $2H_2O$ , and the *barium* salt  $1H_2O$ ; the *silver* salt is somewhat readily soluble in hot water, and resists the action of light.

The three acids yield butylsuccinic acid on reduction with sodium amalgam. A boiling 20 per cent. solution of caustic soda leaves propylitaconic acid for the most part unchanged, giving rise to a small quantity of aticonic acid; propylcitraconic acid yields 43 per cent. of propylitaconic acid, which is also formed in considerable amount when caustic soda acts on propylmesaconic acid. M. O. F.

**Isopropylitaconic Acid and its Isomerides.** By RUDOLPH FITTIG and ARTHUR W. BURWELL (*Annalen*, 1899, 304, 259—280).—The *ethylic* salt of isopropylparaconic acid remains liquid at  $-19^{\circ}$ , and boils at  $282^{\circ}$ .

*Isopropylitaconic acid*,  $CHPr^{\beta}:C(COOH):CH_2\cdot COOH$ , obtained by the action of sodium ethoxide on ethylic isopropylparaconate, separates from water in nacreous crystals and melts at  $189-192^{\circ}$ , when it becomes brown, and liberates gas. The *barium* salt contains  $2H_2O$ , and the *calcium* salt  $1H_2O$ ; the *silver* salt is indifferent towards light.

*Isopropylcitraconic acid*,  $CH_2Pr^{\beta}:C(COOH):CH\cdot COOH$ , obtained in the form of anhydride by distilling isopropylitaconic acid, crystallises from a mixture of chloroform and petroleum in elongated, lustrous needles, and melts at  $78-81^{\circ}$ , forming the anhydride. The *barium* and *silver* salts are anhydrous. When an aqueous solution of the acid is heated at  $150-160^{\circ}$ , it is converted almost completely into isopropylitaconic acid.

*Isopropylmesaconic acid*,  $CH_2Pr^{\beta}:C(COOH):CH\cdot COOH$ , is formed from isopropylcitraconic acid under the influence of bromine, and melts at  $183^{\circ}$ ; it forms crystals belonging to the monoclinic system:  $a:b:c = 1.4268:1:0.7453$ ;  $\beta = 75^{\circ} 40'$ . This acid, which has been

described as oxyheptic acid by Demarçay, is formed in small amount when isopropylcitraconic acid is treated with nitric acid. The *barium* and *calcium* salts are anhydrous.

Boiling caustic soda has no action on isopropylitaconic acid, this substance being produced when isopropylcitraconic acid is treated with a boiling 10 per cent. solution of caustic soda during 30 hours; it is also formed when isopropylmesaconic acid is heated with 25 per cent. caustic soda during 35 hours. *Isobutylsuccinic acid*,  $C_8H_{14}O_4$ , prepared by reducing the three foregoing acids with sodium amalgam, melts at  $107-108^\circ$ , and forms crystals belonging to the rhombic system:  $a:b:c = 0.8551:1:1.0877$ .

*Isopropylisoparaconic acid*,  $\begin{matrix} CMe_2 \cdot CH_2 \\ O \text{---} CO \end{matrix} > CH \cdot CH_2 \cdot COOH$ , is obtained

in the preparation of isopropylitaconic acid from ethylic isopropylparaconate, and is also produced when isopropylitaconic acid is heated with fuming hydrochloric acid at  $125-135^\circ$  during 3 hours; it crystallises from water in large, lustrous, transparent prisms belonging to the monoclinic system:  $a:b:c = 0.6623:1:0.4853$ ;  $\beta = 72^\circ 54'$ . It melts at  $143^\circ$ , and when carefully heated volatilises without decomposing. The *calcium* salt contains  $3\frac{1}{2}H_2O$ , whilst the *barium* and *silver* salts are anhydrous; the *ethylic* salt boils at  $276^\circ$ . Further treatment with alkalis resolves the salts into those of the dibasic dihydroxy-acid,  $C_8H_{14}O_5$ ; the *calcium*, *barium*, and *silver* salts are anhydrous.

Evidence in support of the above constitutional formula for isopropylisoparaconic acid is supplied by the fact that the substance is produced from isobutylsuccinic acid by oxidation with potassium permanganate.

M. O. F.

**Isopropylisoparaconic acid.** By RUDOLPH FITTIG and HEINRICH THRON (*Annalen*, 1899, 304, 280—298. Compare forgoing abstract).—The extraordinary readiness with which isopropylisoparaconic acid is produced on heating isopropylparaconic acid with fuming hydrochloric acid, would seem to indicate the existence of stereoisomerism instead of structural isomerism, but this possibility is precluded by the formation of isopropylisoparaconic acid on oxidising isobutylsuccinic acid with potassium permanganate.

*Isobutylethanedetricarboxylic acid*,  $CH_2Pr^B \cdot C(COOH)_2 \cdot CH_2 \cdot COOH$ , is prepared by treating the sodium derivative of ethylic isobutylmalonate with ethylic chloracetate, and hydrolysing the ethereal salt with alcoholic potash; it crystallises in slender, silky needles on adding petroleum to the solution in ether, and melts at  $156^\circ$ , yielding isobutylsuccinic acid. The *calcium* salt contains  $7H_2O$ , and the *barium* salt  $4H_2O$ ; the *silver* salt is crystalline, and is sensitive towards light.

*Isobutylsuccinic acid*,  $COOH \cdot CH(CH_2Pr^B) \cdot CH_2 \cdot COOH$ , obtained on heating the foregoing acid at  $160^\circ$  until carbonic anhydride ceases to be evolved, separates from water in large, rhombic crystals, and melts at  $107^\circ$ ; as already stated (*loc. cit.*), oxidation converts it into isopropylisoparaconic acid.

Another method of preparing isopropylisoparaconic acid consists in heating isopropylitaconic acid with sulphuric acid. It is also produced by the action of sodium on a mixture of ethylic succinate and isobut-

aldehyde, isopropylitaconic acid being also formed. When boiled in a reflux apparatus during 10 minutes, it yields about 25 per cent. of isopropylcitraconic acid along with a smaller proportion of isopropylitaconic acid.

The acid  $C_{16}H_{20}O_6$ , obtained by heating ethylic isopropylisoparaconate with sodium and ether on the water-bath, crystallises in leaflets containing  $6H_2O$ , and melts at  $222^\circ$ . The *calcium*, *barium*, and *silver* salts are anhydrous, and indicate that the acid is monobasic. The substance is very stable, resisting the action of a boiling 10 per cent. solution of caustic soda during several hours; it undergoes no change when heated at  $230^\circ$ . M. O. F.

**Isobutylitaconic Acid and its Isomerides.** By RUDOLPH FITTIG and CARL SCHIRMACHER (*Annalen*, 1899, 304, 298—311. Compare Fittig and Kräncker, *Abstr.*, 1890, 874).—*Isobutylcitraconic acid*,  $CH_2Pr^{\beta} \cdot CH_2 \cdot C(COOH) : CH \cdot COOH$ , prepared in the form of anhydride by submitting isobutylitaconic acid to dry distillation, crystallises from a mixture of chloroform and petroleum in beautiful, colourless leaflets, and melts at  $75.5-80^\circ$ . When pure, it remains unchanged on exposure to air, but the impure substance is resolved into the anhydride and water (compare Fittig and Weil, *Abstr.*, 1895, i, 207). The *barium*, *calcium*, and *silver* salts are anhydrous.

*Isobutylmesaconic acid*,  $CH_2Pr^{\beta} \cdot CH_2 \cdot C(COOH) : CH \cdot COOH$ , obtained by the action of bromine on isobutylcitraconic acid, crystallises from water in lustrous leaflets, and melts at  $205-206^\circ$ ; the *barium* and *calcium* salts contain  $1H_2O$ , and the *silver* salt is anhydrous.

When isobutylcitraconic acid is heated with water in a sealed tube at  $160^\circ$ , it yields isobutylitaconic acid; the latter is in part converted into isobutylparaconic acid by the agency of hydrobromic acid at  $100^\circ$ .

*Isamylsuccinic acid*,  $CH_2Pr^{\beta} \cdot CH_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$ , prepared by reducing isobutylitaconic acid in feebly acid solution with sodium amalgam on the water-bath, dissolves very readily in water, and melts at  $75-76^\circ$ ; it resembles the citraconic acids more closely than those of the succinic series. The *barium* salt contains  $\frac{1}{2}H_2O$ , and the *calcium* and *silver* salts are anhydrous.

A boiling 10 per cent. solution of caustic soda has no action on isobutylitaconic acid, but gives rise to the latter when boiled with isobutylcitraconic and isobutylmesaconic acids. M. O. F.

**Isobutylaticonic Acid.** By RUDOLPH FITTIG and EDGAR ERLBACH (*Annalen*, 1899, 304, 311—325).—*Isobutylaticonic acid*,  $C_9H_{14}O_4$ , is obtained in small quantities when isobutylitaconic acid is treated with a boiling 20 per cent. solution of caustic soda in a reflux apparatus during 15 hours; it crystallises in elongated prisms when petroleum is added to the solution in ether, and melts at  $95^\circ$ . It is more readily soluble than isobutylitaconic acid, 100 parts of water dissolving 1.863 parts and 0.377 part respectively; 100 parts of ether dissolve 35.60 parts and 3.01 parts respectively. The *barium*, *calcium*, and *silver* salts are anhydrous. The *dibromide*,  $C_9H_{14}Br_2O_4$ , is formed to the extent of 16 per cent. when a solution of bromine in chloroform acts on isobutylaticonic acid in the same medium; it melts and loses hydrogen bromide at  $210^\circ$ .

*Bromisobutylisoparaconic acid*,  $C_9H_{13}BrO_4$ , the chief product of the action of bromine on isobutylitaconic acid, crystallises from ether in silky, lustrous needles, and melts at  $126^\circ$ . *Isobutylisoparaconic acid*,  $C_9H_{14}O_4$ , prepared by reducing the bromo-derivative with sodium amalgam, crystallises from ether in long needles and melts at  $115^\circ$ ; the *barium* salt contains  $1H_2O$ , the *calcium* salt  $2H_2O$ , and the *silver* salt is anhydrous.

*Isobutylisaconic acid*,  $C_9H_{12}O_4$ , obtained by the action of aqueous caustic soda on bromisobutylisoparaconic acid, melts at  $51^\circ$ , and dissolves readily in common solvents; the *barium* salt contains  $4H_2O$ , and the *calcium* salt  $3H_2O$ , whilst the *silver* salt crystallises from hot water in nacreous, anhydrous leaflets.

*Isononodilactone*,  $C_9H_{12}O_4$ , produced along with isobutylisaconic acid on treating bromisobutylisoparaconic acid with boiling water in a reflux apparatus during 5 hours, crystallises from water and melts at  $133^\circ$ ; further treatment with boiling water converts the dilactone into isobutylisaconic acid.

When isobutylitaconic acid is heated with a 10 per cent. aqueous solution of caustic soda in a reflux apparatus during 10 hours, it is converted into isobutylitaconic acid to the extent of about 60 per cent.  
M. O. F.

**Hexylitaconic Acid and its Isomerides.** By RUDOLPH FITTIG and WILLIAM D. HOEFFKEN (*Annalen*, 1899, 304, 326—339).—The *ethylic* salt of hexylparaconic acid is a viscous liquid which boils at  $325$ — $326^\circ$ .

*Hexylitaconic acid*,  $C_6H_{13}\cdot CH\cdot C(COOH)\cdot CH_2\cdot COOH$ , obtained by heating ethylic hexylparaconate with alcoholic sodium ethoxide, and hydrolysing the product, crystallises from water in silky needles, and melts at  $129$ — $130^\circ$ ; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains  $2H_2O$ . On heating the acid with hydrobromic acid during 32 hours at the temperature of boiling water, it is in part converted into hexylparaconic acid.

*Hexylcitraconic acid*,  $C_6H_{13}\cdot CH_2\cdot C(COOH)\cdot CH\cdot COOH$ , prepared by heating the foregoing acid at  $205$ — $210^\circ$  and hydrolysing the anhydride obtained, crystallises in aggregates of needles and melts at  $86^\circ$ ; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains  $1H_2O$ . When heated with water in a sealed tube at  $160^\circ$ , hexylcitraconic acid is converted into hexylitaconic acid.

*Hexylmesaconic acid*,  $C_6H_{13}\cdot CH_2\cdot C(COOH)\cdot CH\cdot COOH$ , produced by the action of bromine on hexylcitraconic acid, dissolves in cold water with great difficulty, and melts at  $153$ — $154^\circ$ ; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains  $1H_2O$ .

When hexylitaconic acid is heated with a 10 per cent. solution of caustic soda, about 70 per cent. remains unchanged, the rest becoming converted into the acid  $C_{11}H_{18}O_4$ , which is isomeric with hexylitaconic acid, and melts at  $70$ — $74^\circ$ ; the same agent converts hexylcitraconic and hexylmesaconic acids into hexylitaconic acid.

*Heptylsuccinic acid*,  $C_6H_{13}\cdot CH_2\cdot CH(COOH)\cdot CH_2\cdot COOH$ , prepared by reducing the three isomeric acids with sodium amalgam, crystal-

lises from water and melts at 90—91°; the *barium* and *silver* salts are anhydrous, and the *calcium* salt contains 1H<sub>2</sub>O. M. O. F.

**Cineolic Acid.** By HANS RUPE (*Chem. Centr.*, 1898, ii, 1055; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 388—390).—When cineolic acid,  $\text{COOH} \cdot \text{CMe} \begin{smallmatrix} \text{O} - \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{COOH}$ , is heated with water at 160°, it

yields *cineolenic acid*,  $\text{CHMe} \begin{smallmatrix} \text{O} - \text{CMe}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{COOH}$ , and another acid of the same empirical formula. The former crystallises in plates or prisms, melts at 83—84°, boils at 127·5—129·5° under 13 mm., and at 250° under 760 mm. pressure; as it is not attacked by bromine or potassium permanganate, it probably contains the cineol chain.

The second acid,  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CMe}_2 \cdot \text{OH}$ , crystallises from water, in which it is much more soluble than cineolenic acid, in small needles, melts at 53—54°, and boils at 158—160° under 13 mm. pressure; its magnesium salt is insoluble in cold water. This acid is also obtained by heating cineolenic acid with water at 150°, and cannot contain the cineol chain, as it is attacked by bromine and potassium permanganate. When distilled under the ordinary pressure, it loses 1H<sub>2</sub>O and yields a new liquid acid,  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CMe} \cdot \text{CH}_2$ , hence it probably contains an OH-group in the  $\beta$ -position. E. W. W.

**Polymerisation of Hydroaromatic Ketones.** By EMIL KNOEVENAGEL and E. REINECKE (*Ber.*, 1899, 32, 418—428).—Ethylic  $\beta$ -methylamidocrotonate readily unites with ethylic ethylideneacetoacetate at 0° to form *ethylic  $\beta$ -methylamidocrotonoethylideneacetoacetate*,  $\text{NHMe} \cdot \text{CMe} \cdot \text{C}(\text{COOEt}) \cdot \text{CHMe} \cdot \text{CHAc} \cdot \text{COOEt}$ , which crystallises from light petroleum in well-formed, transparent prisms, melts at 103—104°, and is readily soluble in alcohol, ether, and benzene; when this is boiled for 2—3 hours with 70 per cent. aqueous potash, it gives rise to a *substance*, C<sub>8</sub>H<sub>12</sub>O, which crystallises from light petroleum in tufts of needles, melts at 113°, boils unchanged at 185—188° under 11 mm. pressure, and with partial decomposition at 258—262° under the ordinary pressure. The same product is also obtained on boiling ethylic ethylidenebisacetoacetate, ethylic 1:3-dimethyl-5-cyclohexenone-2:4-dicarboxylate, or 1:3-dimethyl-5-cyclohexenone with 70 per cent. aqueous potash; from molecular weight determinations by the cryoscopic and boiling point methods, it appears to be dimeric with the latter of these, and the formula  $\text{CH}_2 \begin{smallmatrix} \text{CMe} = \text{CH} \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CO} - \text{CH} \end{smallmatrix} \text{CMe}$  is attributed to it, assuming that it is formed according to the laws governing the polymerisation of open-chain ketones. In accordance with this view are the facts that it yields a *monoxime*, C<sub>16</sub>H<sub>25</sub>NO<sub>2</sub>, and a *monophenylhydrazone*, C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>O, only, without forming a dioxime or a diphenylhydrazone; the former of these separates from dilute alcohol in yellow crystals and melts at 197°, whilst the latter crystallises from alcohol in white needles and melts at 202—204°; the *semicarbazone* melts at 212°. The assumption of the presence of a

hydroxyl group, however, is not borne out by the behaviour of the compound with acetic anhydride or phenylcarbimide, since both of these are without action; phosphorus pentoxide, zinc chloride, and 30 per cent. sulphuric acid also seem incapable of causing a separation of water to form a substance of the type of mesityl oxide.

1-Methyl-5-cyclohexenone remains unchanged when heated with 70 per cent. aqueous potash, but ethylic benzylidenedisacetoacetate and 1-methyl-3-phenyl-5-cyclohexenone both give rise to the same substance,  $C_{26}H_{28}O_2$ , which crystallises from alcohol, melts at  $159^\circ$ , is sparingly soluble in ether, chloroform, light petroleum, and benzene, and yields an oxime,  $C_{26}H_{29}NO_2$ , which crystallises from alcohol and melts at  $207^\circ$ ; the *phenylhydrazone* crystallises from benzene and melts at  $250-251^\circ$ . 1-Methyl-3-isopropylphenyl-5-cyclohexenone gives rise, when treated with alkali, to the *polymeride*,  $C_{32}H_{40}O_2$ , which crystallises from light petroleum, melts at  $175^\circ$ , and is easily soluble in chloroform and benzene.

W. A. D.

**Action of Iodine Chloride on Chlorobenzene in presence of Aluminium Chloride.** By A. MOUNEYRAT (*Compt. rend.*, 1899, 128, 240—242).—When iodine chloride acts on monochlorobenzene in presence of dry aluminium chloride at  $55-60^\circ$ , parachloriodobenzene is obtained in quantity amounting to from 25 to 30 per cent. of the calculated yield, small quantities of dichlorobenzene and trichlorobenzene being formed at the same time.

C. H. B.

**1:3:5-Tribromo-2:4:6-tri-iodobenzene.** By CONSTANTIN I. ISTRATI (*Compt. rend.*, 1898, 127, 519).—When a mixture of 1:3:5-tribromobenzene with concentrated sulphuric acid is heated with iodine for six or seven days, a mixture of iodine derivatives is obtained, from which, by successive treatment with various solvents, 1:3:5-tribromo-2:4:6-tri-iodobenzene may be isolated. This crystallises in small, golden-yellow needles melting at  $322^\circ$ , and is dissolved by boiling chloroform and boiling alcohol to the extent of 0.306 and 0.040 per cent. respectively. It is attacked with difficulty by fuming nitric acid, but, in presence of sulphuric acid, yields a mixture of nitro-derivatives containing 4.07 per cent. of nitrogen. Cold alcoholic potash, whilst not destroying the original form of the crystals, immediately converts them into a greyish-yellow substance which does not contain iodine, and is insoluble in ordinary solvents.

N. L.

**Action of Hydrogen Chloride and Hydrogen Bromide on Nitrosoaliphyls.** By EUGEN BAMBERGER, HANS BÜSDORF, and B. SZOLAYSKI (*Ber.*, 1899, 32, 210—221).—The chief products of the action of hydrogen chloride on nitrosobenzene are paradichloroxybenzene, 2:4:6-trichloraniline, 2:4-dichloraniline, parachloraniline, parachlorophenylhydroxylamine, resins, and colouring matters, the reactions taking place being of three kinds.

I. An aldol condensation with the elements of hydrogen chloride to form phenylchlorhydroxylamine which, at the moment of its formation, passes into parachlorophenylhydroxylamine.

II. The further action of the halogen acid on phenylchlorhydroxyl-

amine to form exo-dichloraniline, which instantly passes into the isomeric 2 : 4-dichloraniline.

III. The halogen acid, combining both the properties of the hydrogen and the halogen, acts both as a reducing and a halogenating (that is, oxidising) agent, forming in this way phenylhydroxylamine, which passes into parachloraniline and azoxybenzene, the latter being converted into dichlorazoxybenzene by the further action of the halogen acid.

Hinsberg has shown that aliphylsulphinic acids react with nitroso-compounds in the same way as halogen acids, and the fact that the additive product,  $\text{OH} \cdot \text{NPh} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$ , is formed when nitrosobenzene is treated with paratolylsulphinic acid is an argument in favour of the intermediate formation of phenylchlorhydroxylamine in the above reactions.

With nitrosotoluene, the reaction is very similar, only in this case the presence of phenols can be detected; their formation being evidently due to the denitrating action of the mineral acid,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NO} + \text{HCl} = \text{C}_6\text{H}_5\text{Me} + \text{NOCl}$ , the latter acting as a diazotising agent, converting a part of the nitrosotoluene into a salt of diazotoluene which yields the cresols and halogenated cresols under the influence of the halogen acid.

The paper concludes with a table giving the comparative weights of the various substances obtained. J. F. T.

**Phenylphosphoric and Phenylenephosphoric Acids.** By P. GENVRESSE (*Compt. rend.*, 1898, 127, 522—523).—Phenylphosphoric acid,  $\text{PO}_4\text{H}_2\text{Ph}$  (compare Belugou, *Abstr.*, 1898, ii, 558), obtained by heating together phosphoric anhydride and phenol in molecular proportion, forms white crystals, slowly becoming grey, which melt at  $89^\circ$ , are very hygroscopic, and are very soluble in water and alcohol, insoluble in benzene. Belugou's observations on the behaviour of the acid towards indicators are confirmed. Phenylphosphoric acid gives a slightly bluish-white precipitate with a neutral solution of cupric acetate, but is not directly precipitated by ammonium molybdate in nitric acid solution except after previous treatment with potash.

*Phenylenediphosphoric acid*,  $\text{C}_6\text{H}_4(\text{PO}_4\text{H}_2)_2$  [ $\text{PO}_4\text{H}_2 : \text{PO}_4\text{H}_2 = 1 : 4$ ], obtained by the action of phosphoric anhydride on quinol, forms crystals melting at  $168$ — $169^\circ$  which are very soluble in water, alcohol, and ether, but insoluble in benzene. It is very hygroscopic, is not a reducing agent, gives a greenish precipitate with cupric acetate, is not directly precipitated by ammonium nitromolybdate, and yields quinol on treatment with potash. It behaves like phenylphosphoric acid towards the indicators helianthin and phenolphthalein.

*Hydroxyphenylphosphoric acid*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{PO}_4\text{H}_2$  [ $\text{PO}_4\text{H}_2 : \text{OH} = 1 : 2$ ], prepared by heating phosphoric anhydride with catechol under diminished pressure and subsequently distilling, crystallises in fine needles melting at  $139^\circ$ ; like the preceding compounds, it is very hygroscopic, very soluble in water and alcohol, and insoluble in benzene. It is vigorously attacked by fuming nitric acid, yields a green precipitate with ammonium nitromolybdate, and is decomposed



by potash with the formation of catechol and potassium phosphate. It reduces Fehling's solution after some time, and silver nitrate solution on heating, and is distinguished from other phenols by yielding a red colouring matter when treated with the diazo-derivative of 1 : 4-sulphanilic acid. N. L.

**Isomeric Tribromo-derivatives of Pseudocumenol.** By KARL AUWERS (*Ber.*, 1899, 32, 17—26).—The isomeric tribromo- $\psi$ -cumenol, obtained in the bromination of  $\psi$ -cumenol (Abstr., 1896, i, 423; 1897, i, 35; 1898, i, 647, 648), is now shown to be identical with tribromoparaxylenol (this vol., i, 35); reduction with 2 per cent. sodium amalgam converts it into paraxylenol. The true melting point of tribromoparaxylylic benzoate, which is best prepared by the method of Einhorn and Hollandt (Abstr., 1898, i, 578), is 126—127°. *Paraxylylic phenylcarbamate* (*paraxylenol carbanilate*),  $\text{NHPh}\cdot\text{COO}\cdot\text{C}_6\text{H}_3\text{Me}_2$ , obtained by heating paraxylenol with phenylic cyanate in benzene solution for 3 hours at 100°, melts at 160—161°; the corresponding  $\psi$ -cumylyc and mesitylyc salts melt at 110—111° and 140—142° respectively.

An isomeric tribromo- $\psi$ -cumenol has, however, been obtained in the following manner. The diacetyl derivative of the compound  $\text{C}_9\text{H}_{10}\text{Br}_2\text{O}_2$ , obtained by heating the nitro-compound from dibromo- $\psi$ -cumenol in glacial acetic acid (this vol., i, 30), is dissolved in acetic acid and gaseous hydrogen bromide is passed in at the ordinary temperature, when a *tribromo- $\psi$ -cumylyc acetate*,  $\text{OAc}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$ , melting at 105—106°, is obtained, which is converted by gaseous hydrogen bromide at a higher temperature into a new *tribromo- $\psi$ -cumenol*,  $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\text{Br}$ , or  $\text{C}_6\text{HMe}_2\text{Br}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}$  (Abstr., 1898, i, 646);

this melts at 128°, and resembles its isomeride in its properties and reactions, except that the reactions take place more slowly. It is insoluble in alkalis, but is decomposed by them; one of the bromine atoms is removed under the influence of various reagents; with boiling methylic alcohol, the *methylyc ether*,  $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OMe}$ , melting at 106° and soluble in aqueous alkalis, is formed; with sodium acetate and acetic acid, the *monacetate*,  $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OAc}$ , melting at 106° and soluble in, but eventually decomposed by, cold alkalis; with acetone and water, the *phenol-alcohol*,  $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$ , melting at 154—155°. The last substance is better prepared by hydrolysing the diacetyl compound mentioned above with alcoholic potash; it is reconverted into that compound by boiling with acetic anhydride, and gaseous hydrogen bromide converts it into the tribromo- $\psi$ -cumenol melting at 128°. Possibly these compounds are derivatives of the orthophenol-alcohol, those previously known being para-derivatives.

C. F. B.

**Action of Nitrous Acid on Resorcinol Monethylic Ether.** By CARL KIETAIBL (*Monatsh.*, 1898, 19, 536—556).—The monethylic ether of resorcinol (metethoxyphenol), in whatever way prepared, is always accompanied by the diethylic ether and unaltered resorcinol; the best process is to dissolve resorcinol in ether, add sodium ethoxide, and evaporate until the residue has a pasty consistency; ethylic

iodide is then added, and the whole heated on a water-bath until the alkalinity has disappeared; the monethylic ether is isolated by acidifying, extracting with ether, and distilling the oil obtained in a current of steam; the two ethers are thus volatilised and may be separated by means of alkali.

Resorcinol monethylic ether is a thick, pale yellow liquid, sparingly soluble in water, readily in the other common solvents, and distils at  $246-247^{\circ}$  (uncorr.) under atmospheric pressure; it darkens rapidly on exposure to air.

When resorcinol monethylic ether (15 grams) is dissolved in a mixture of alcohol (28 grams) and acetic acid (25 grams) and treated cautiously, at a temperature not exceeding  $-1^{\circ}$ , with a solution of sodium nitrite (10 grams) in water (20 c.c.), a red substance, *a*, is soon deposited and may be immediately separated by filtration, whilst from the mother liquor a second crop of crystals, *b*, is obtained, which may be collected after the lapse of 12 hours; the mother liquor, on dilution, deposits a third portion, *c*, of solid matter.

The solid *a* consists of a mixture of  $\alpha$ - and  $\beta$ -orthonitroso- with para-nitroso-resorcinol monethylic ether; these may be separated by extraction with benzene, which leaves the para-compound undissolved, and on cooling deposits the  $\alpha$ -orthonitroso-derivative in a fairly pure state, leaving the  $\beta$ -derivative in solution.

*$\alpha$ -Orthonitrosoresorcinol monethylic ether*,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{OH}$ , is sparingly soluble in water but readily in alcohol, ether, and benzene; it crystallises from the last-named liquid in golden-yellow, shining needles melting at  $133.5^{\circ}$  (uncorr.), and gives Liebermann's nitroso-reaction. The *potassium* derivative,  $\text{C}_8\text{H}_8\text{NO}_3\text{K}$ , is sparingly soluble in hot alcohol, and crystallises in slender, olive-green, glistening needles; when exposed to moisture or air, it becomes red, but reverts to the original tint if heated at  $100^{\circ}$ ; the *sodium* salt is similar. The aqueous solutions of these salts give a brownish-red precipitate with silver nitrate, and a cherry-red precipitate with mercuric chloride.

*$\alpha$ -Orthamidometethoxyphenol hydrochloride*,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NH}_2 \cdot \text{HCl}$ , obtained from the above compound by reduction with stannous chloride and hydrochloric acid, forms colourless prisms which quickly turn violet on exposure to air, and when heated decompose without melting; its aqueous solution gives a red coloration with ferric chloride.

*$\alpha$ -Orthamidometethoxycarbonylphenol*,  $\text{C}_7\text{H}_4\text{NO}_2\text{OEt}$ , crystallises from benzene in colourless needles, dissolves readily in most of the ordinary solvents, and melts at  $150.5-151.5^{\circ}$  (uncorr.).

*$\beta$ -Orthonitrosoresorcinol monethylic ether*,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{OH}$ , dissolves readily in alcohol, benzene, and ether, and crystallises from the last-mentioned liquid in slender needles melting at  $102^{\circ}$  (uncorr.); it gives Liebermann's reaction. The *potassium* and *sodium* derivatives are red; the *silver* salt,  $\text{C}_8\text{H}_8\text{NO}_3\text{Ag}$ , is a reddish-brown, crystalline precipitate; on addition of mercuric chloride to the aqueous solution of the sodium salt, a cherry red precipitate is obtained.

*$\beta$ -Orthamidometethoxyphenol hydrochloride*,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{NH}_2 \cdot \text{HCl}$ , crystallises in colourless prisms which quickly become violet coloured on exposure to air; it is readily soluble in water, alcohol, and dilute

hydrochloric acid, but only sparingly in strong hydrochloric acid; its aqueous solution gives no coloration with ferric chloride. It differs from the  $\alpha$ -nitroso-compound in its behaviour towards potash or ammonia, its solution being coloured red on addition of the former, whilst the latter throws down a flocculent, white precipitate; the solution of the  $\alpha$ -derivative, on the other hand, is coloured brown in both cases.  $\beta$ -*Orthamidometethoxycarbonylphenol*,  $C_9H_9O_3N$ , crystallises in white needles and melts at  $125^\circ$  (uncorr.).

The orthonitrosoresorcinol monethylic ethers have the constitution  $[OH:NO:OEt=1:2:3 \text{ and } 1:6:3]$ , but it has not hitherto been possible to decide which of these represents the  $\alpha$ - and which the  $\beta$ -derivative.

*Paranitrosoresorcinol monethylic ether*,  $OEt \cdot C_6H_3(NO) \cdot OH$   $[OH:OEt:NO=1:3:4]$ , may be purified by crystallisation from absolute alcohol, when it is obtained in pale yellow needles; it is very sparingly soluble in water, ether, and benzene, but only sparingly so in boiling alcohol. When heated, it darkens at  $160$ — $170^\circ$ , and is completely decomposed below  $210^\circ$ . It gives Liebermann's reaction. This substance appears to be identical with a product obtained by Aronheim (Abstr., 1878, 465) and by Kraus (Abstr., 1892, 44) from the product of interaction of nitrous acid and resorcinol diethylic ether. The sodium salt is a greyish-green, crystalline substance, which, on exposure to air, becomes lighter in tint, but at  $100^\circ$  resumes its original colour. The aqueous solution of the sodium salt gives, with silver nitrate, an orange-yellow, and with mercuric chloride, a cherry-red precipitate.

*Paramidometethoxyphenol hydrochloride*,  $OEt \cdot C_6H_3(OH) \cdot NH_2 \cdot HCl$ , crystallises in large, colourless needles, which become violet on exposure to the air, and when heated decompose without melting. Ferric chloride produces a violet coloration in its aqueous solution. The crystals belong to the rhombic system, the axial ratio being approximately  $a:b:c=0.8616:1:0.5899$ . It does not give a carbonyl derivative when heated with carbamide, and when oxidised with sodium chromate yields ethoxyquinone.

A fourth substance may be isolated from  $b$  and  $c$ ; this melts at  $176^\circ$ , dissolves sparingly in boiling water, more readily in alcohol, ether, and ethylic acetate, and crystallises from hot alcohol in silky, greenish-yellow needles; it gives Liebermann's reaction. Its composition is nearly expressed by the formulæ  $C_{16}H_{18}N_2O_5$  or  $C_{16}H_{20}N_2O_5$ , which are not, however, in agreement with its observed molecular weight ( $170$ — $190$ ) as determined in melted phenol or boiling ether, or with the analysis of a hydrochloride which is produced on reducing it with stannous chloride. It is possible, therefore, that the substance is not homogeneous. A. L.

**Mesityl Oxide and Ethylic Malonate.** By DANIEL VORLÄNDER (*Ber.*, 1899, 32, 245. Compare Crossley, *Proc.*, 1899, 15, 52).—The condensation products recently described by Crossley (*Proc.*, 1898, 14, 247) have already been examined by Vorländer (*Abstr.*, 1897, i, 275, 276) and have been shown to be derivatives of dihydroresorcinol; the oxidation products have also been examined (this vol., i, 259).

T. M. L.

**Derivatives of Catechol.** By H. COUSIN (*Ann. Chim. Phys.*, 1898, [vii], 480—533. Compare Abstr., 1892, 1443; 1893, i, 258, 637; 1894, i, 368; 1895 i, 456).—A detailed account of work already published.  
G. T. M.

**Separation of the Dimethylic Ethers of Pyrogallol and of Methylpyrogallol.** By OTTO ROSAUER (*Monatsh.*, 1898, 19, 557—570).—Commercial pyrogallol dimethylic ether, as supplied by Schuchardt, is a somewhat complex mixture. In order to effect the separation of the constituents, it was distilled, and the two fractions boiling at 250—260° and 260—270° treated separately. The portion of lower boiling point was treated, in benzene solution, with sodium and ethylic chloroformate, the liquid separated by filtration from sodium chloride, and then evaporated; the crystals which were deposited were separated by fractional distillation into a portion boiling at 183° under 50 mm. pressure, and another portion boiling at 191° under 20 mm. pressure.

*Pyrogallol dimethylic ether ethylic carbonate*,  $\text{COOEt} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ , the crystalline constituent boiling at 183° under 50 mm. pressure, is deposited from methylic alcohol in colourless, prismatic crystals, melts at 63—65°, is volatile in steam, and dissolves very readily in the ordinary solvents, with the exception of light petroleum. When boiled with baryta water, it is decomposed, forming pyrogallol dimethyl ether, which yields pyrogallol when heated with hydriodic acid.

The portion boiling at 191° under 20 mm. pressure, is *methylpyrogallol dimethylic ether ethylic carbonate*,  $\text{COOEt} \cdot \text{O} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OMe})_2$ ; it crystallises from alcohol in short, colourless, prismatic needles melting at 111—113°. It is nearly insoluble in boiling water, and is only sparingly soluble in light petroleum, but dissolves readily in ether, benzene, and hot alcohol, and is volatile in steam. Methylpyrogallol dimethylic ether,  $\text{C}_6\text{H}_2\text{Me}(\text{OMe})_2 \cdot \text{OH}$ , produced when the foregoing substance is boiled with baryta water, melts at 29—30°, boils at 145—146° under 12 mm. pressure, and dissolves somewhat readily in water and in the usual solvents; ferric chloride imparts a violet colour to the aqueous solution. Methylpyrogallol crystallises from benzene in slender, colourless, felted needles, and melts at 116—119°; its aqueous solution is coloured bluish-violet by ferric chloride, whilst, with alkalis, it gives a bright yellowish-red, which slowly becomes dark brownish-red. With ferrous sulphate, it behaves like pyrogallol and when fused with potash it yields gallic acid. The author concludes that methylpyrogallol dimethylic ether is identical with that obtained by Hofmann, and therefore has the constitution  $\text{Me}:\text{OH}:(\text{OMe})_2 = 1:3:5:4$ . *Methylpyrogallol triacetate*,  $\text{C}_6\text{H}_2\text{Me}(\text{OAc})_3$ , prepared by heating methylpyrogallol with acetic anhydride at 134°, crystallises from a mixture of benzene and petroleum in yellowish tablets, which, perhaps, belong to the triclinic system, the axial ratio being  $a:b:c = 1.19:1:1.54$ ,  $ac = 90^\circ 44'$ .  
A. L.

**Nitration of Guaiacol.** By GUSTAV KOMPPA (*Chem. Centr.*, 1898, ii, 1169; from *Oefversigt af Finska Vet.-Soc. Förhandlingar*, 40).—When an ice-cold solution of guaiacol in glacial acetic acid is treated with an ice-cold mixture of 1 volume of fuming nitric acid with 4

volumes of glacial acetic acid, water then added, and the liquid distilled with steam, yellow crystals which melt at  $65^{\circ}$  and are, perhaps, mononitroguaiacol, separate from the distillate. The non-volatile residue yields Herzig's dinitroguaiacol (Abstr., 1883, 464). The *acetyl* derivative,  $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{OAc}$ , crystallises in yellowish plates, and melts at  $114^{\circ}$ ; it is rather easily soluble in hot, but only slightly so in cold, alcohol, and is insoluble in water. E. W. W.

**Synthesis of Asarone.** By LUDWIG GATTERMANN and F. EGGERS (*Ber.*, 1899, 32, 289—291).—When 1 : 2 : 4-trimethoxybenzene is acted on by hydrogen cyanide in presence of hydrogen chloride and aluminium chloride (compare Abstr., 1898, i, 476 and 581), it is converted into 1 : 2 : 4 : 5-trimethoxybenzaldehyde; the identity of this with asaric aldehyde obtained from asarone by oxidation is shown by its melting point, by the properties of its azine, and by its yielding asaronic acid when oxidised with potassium permanganate. When the aldehyde (2 grams) is heated with propionic anhydride (3 grams) and sodium propionate (1 gram) during 7 hours at  $150^{\circ}$ , it is converted, to the extent of 60 per cent., into asarone; the latter is therefore shown to be 1 : 2 : 4 : 5-trimethoxypropenylbenzene,  $\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_2(\text{OMe})_3$ . The view that the aldehyde from which it was obtained contains the CHO-group in position 5 is justified by its method of preparation, which, according to all analogous instances (*loc. cit.*), necessitates this group being in the para-position relatively to the methoxyl. Together with asarone, there is formed in the above synthesis a small quantity of trimethoxy- $\alpha$ -methylcinnamic acid,  $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CH} : \text{CMe} \cdot \text{COOH}$ , as an intermediate product; this separates from alcohol in stout, colourless crystals, and melts at  $157^{\circ}$ . W. A. D.

**Oxidation Products of Diquinoyltetroxime.** By RUDOLPH NIETZKI and W. GEESE (*Ber.*, 1899, 32, 505—507).—1 : 2 : 3 : 4-Tetranitrosobenzene,  $\text{C}_6\text{H}_2(\text{NO})_4$ , prepared by adding sodium hypochlorite to a solution of diquinoyltetroxime in concentrated sodium carbonate, crystallises from alcohol in colourless needles, and melts at  $93^{\circ}$ ; reduction with stannous chloride converts it into tetramidobenzene.

Nitrotetranitrosobenzene,  $\text{NO}_2 \cdot \text{C}_6\text{H}(\text{NO})_4$ , obtained by the action of fuming nitric acid, crystallises from alcohol or from acetic acid in yellow needles, and melts at  $158^{\circ}$ .

2 : 3-Dinitrosoquinoneoxime,  $\text{C}_6\text{H}_2(\text{NO})_2(\text{NOH})_2$ , produced on oxidising diquinoyltetroxime with nitric acid, crystallises from alcohol in needles, and melts at  $68^{\circ}$ . M. O. F.

**Oxidation of Aromatic Compounds.** By WILLIAM ECHSNER DE CONINCK and A. COMBE (*Compt. rend.*, 1899, 128, 239—240).—When orthamidophenol, paramidophenol, the three amidobenzoic acids, ortho- and para-nitrophenol, paranitrotoluene, picric acid, benzamide, salicylamide, and hydrobenzamide are oxidised with chromic mixture, no nitrogen is liberated. Picramic acid, on the other hand, yields a small quantity of nitrogen as well as carbonic anhydride. C. H. B.

**Oxidation of Aromatic Bases.** By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, 32, 342—355).—When aniline, in

sulphuric acid solution, is oxidised with potassium permanganate in presence of a small quantity of formaldehyde, it gives rise to nitrobenzene, azoxybenzene, and paradiamidodiphenylmethane; in addition to nitrosobenzene, which is the principal product (Abstr., 1898, i, 518). Phenylhydroxylamine is probably formed initially, but cannot be isolated owing to the ease with which it is oxidised to nitrosobenzene. From the experiments which follow, the authors conclude that the first step in the oxidation is the formation of the additive compound,  $C_6H_5 \cdot NH_2 \cdot O$ , which immediately undergoes isomeric change to form phenylhydroxylamine.

Aqueous hydrogen peroxide acts only very slowly on dimethylaniline in the cold; when, however, the base (50 grams) is strongly agitated with the oxidising agent (1410 c.c. of a 3.2 per cent. solution) for 12 hours at 60—70°, it is almost completely converted into *dimethylaniline oxide*,  $NPhMe_2 \cdot O$ , which can be precipitated as the *picrate*,  $NPhMe_2 \cdot O, C_6H_3N_3O_7$ ; this crystallises in sulphur-yellow, monosymmetric needles having a silky lustre, melts at 137—138°, and decomposes at a slightly higher temperature; it is converted by warm, concentrated hydrochloric acid into the *hydrochloride*,  $C_8H_{11}NO, HCl$ , which forms transparent, lustrous, deliquescent prisms, melts and decomposes at 124—125°, and when treated with moist silver oxide, gives rise to the *base*,  $C_8H_{11}O$ . This crystallises in beautiful, colourless, deliquescent prisms, has a bitter taste, softens at about 146°, melts at 152—153°, and is decomposed at a slightly higher temperature with the production of dimethylaniline, which is also obtained when hydrogen sulphide is passed through an aqueous solution of the oxide, or when the latter is reduced with zinc and hydrochloric acid. Unlike triethylamine oxide,  $NEt_3 \cdot O$  (Bewad, Abstr., 1889, 112), dimethylaniline oxide has no reducing properties, and is stable in presence of dilute alkalis, whilst it differs from the alkylpiperidine oxides (Merlin, Abstr., 1893, i, 113; Wernick and Wolfenstein, Abstr., 1898, i, 536) in not liberating iodine from potassium iodide. The *platinochloride*,  $(C_8H_{11}NO)_2, H_2PtCl_6 + nH_2O$ , crystallises from water in orange-red, lustrous, rhombic plates, and melts, after being dried in a vacuum over sulphuric acid, indefinitely at 136—137°, and decomposes at 146°; the *aurichloride*,  $C_8H_{11}NO, HAuCl_4$ , forms lustrous, yellow needles, and is somewhat sparingly soluble in water, whilst the *ferrocyanide*,  $(C_8H_{11}NO)_2, H_2FeC_6N_6$ , is a white, crystalline powder, which, when heated, explodes at 144.5°. When dimethylaniline oxide is acted on by nitrous acid, it gives rise principally to ortho- and para-nitrodimehtylaniline; this is explained by assuming that nitrosodimehtylaniline oxide,  $NO \cdot C_6H_4 \cdot NMe_2 \cdot O$ , is first formed, and then undergoes isomeric change. When the hydrochloride of the base is warmed on the water-bath for several hours with an excess of benzaldehyde, malachite-green is formed without it being necessary to employ a dehydrating agent.

*Diethylaniline oxide*,  $NPhEt_2 \cdot O$ , is formed, together with formic acid and other substances, by the action of hydrogen peroxide on diethylaniline; the *picrate*,  $C_{16}H_{18}N_4O_8$ , separates from alcohol in dark yellow prisms resembling salt crystals. The *picrates*,  $C_{15}H_{16}N_4O_8$ , of dimethylortho- and dimethylpara-toluidine oxides crystallise in

yellow needles, and melt at  $145.5$ — $146.5^\circ$  and  $106$ — $107^\circ$  respectively.

W. A. D.

**Action of Alcoholic Hydrogen Chloride on Nitrosophenylglycine [Nitrosoanilidoacetic Acid].** By OTTO FISCHER (*Ber.*, 1899, 32, 247—249. Compare *Abstr.*, 1887, 1115).—When nitrosoanilidoacetic acid is boiled with water, it is decomposed into carbonic anhydride and nitrosomethylaniline; the alkali salts, however, are stable. The *ammonium* salt crystallises in pearly flakes and dissolves readily in water; the *phenylhydrazine* salt separates from alcohol, in which it is only slightly soluble, in beautiful, white flakes, and melts at  $124^\circ$ ; the *ethylic* salt is a brownish-yellow oil.

By the action of alcoholic hydrogen chloride on nitrosoanilidoacetic acid or its ethylic salt, an explosive substance is produced which is regarded as the chloride of paradiazophenylhydroxylamine,  $\text{OH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$  (Fischer and Hepp, *loc. cit.*). The *aurichloride*,  $\text{C}_6\text{H}_5\text{N}_3\text{O}\cdot\text{HAuCl}_4$ , which crystallises in reddish needles, is decomposed by cold water, but not by concentrated hydrochloric acid. The *sulphate* forms yellow needles and is somewhat more stable. The addition of phenylhydrazine to the dry chloride causes it to explode, whilst in concentrated alcoholic or ethereal solution there is a vigorous evolution of nitrogen; in dilute solution, the hydrochloride of phenylhydrazine is slowly deposited. Diazophenylhydroxylamine has not been converted either into phenylhydroxylamine or into nitrosobenzene, but by warming its alcoholic solution or by acting on it with copper powder, nitrogen is evolved and azoxybenzene produced.

T. M. L.

**Maleic Derivatives of some Aromatic Amines.** By ERCOLE GIUSTINIANI (*Gazzetta*, 1898, 28, ii, 189—192).—The author proposes extending the method employed by Giustiniani and Piutti for preparing maleic derivatives of fatty monamines and of benzylamine to other aromatic amines with a view of finding a good method for preparing substituted maleimides.

T. H. P.

**Orthobromoparanisidine.** By ALBERTO BENEVENTO (*Gazzetta*, 1898, 28, ii, 202—208).—Staedel prepared orthobromoparanisidine by reducing orthobromoparanitranisole and described it as an oil. The author has obtained it crystalline by the following method: paranisidine and succinic acid, heated together, give paramethoxyphenylsuccinimide, the orthobromo-derivative of which, on treatment with hydrochloric acid, yields acicular crystals of the hydrochloride of orthobromoparanisidine. The base forms yellowish crystals melting at  $60$ — $61^\circ$ ; it is soluble in hot water, ether, alcohol, and ethylic acetate, and is stable to light. The *sulphate*, *oxalate*, and *succinate* were prepared, the last named forming acicular crystals melting at  $61^\circ$ .

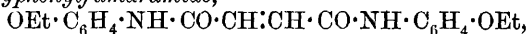
T. H. P.

**Action of Malic Acid on Paramidophenetoil.** By G. CAMPANARO (*Gazzetta*, 1898, 28, ii, 192—197).—Amidophenetoil *hydrogen malate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OEt}\cdot\text{COOH}\cdot\text{C}_2\text{H}_3(\text{OH})\cdot\text{COOH}$ , is readily obtained by the combination of malic acid and paramidophenetoil, and separates from hot water in white crystals melting at  $150^\circ$ ; on heating, it

loses a molecule of water, forming *parethoxyphenylmalamic acid*,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_2\text{H}_3(\text{OH}) \cdot \text{COOH}$ , which, when purified by crystallisation from hot water, is obtained in small, yellowish needles melting at  $160^\circ$ , and is very soluble in hot water, alcohol, and ether. The *silver* salt,  $\text{C}_{12}\text{H}_{14}\text{AgNO}_5$ , was prepared, and the *barium* salt,  $(\text{C}_{12}\text{H}_{14}\text{NO}_5)_2\text{Ba}$ , forms splendid, white, acicular crystals. The *ethyllic* salt,  $\text{C}_{12}\text{H}_{14}\text{EtNO}_5$ , is crystalline and melts at  $235^\circ$ ; it is very soluble in water, less so in alcohol and ether.

*Acetyllethoxyphenylmalamic acid*, obtained by the action of acetic anhydride on ethoxyphenylmalamic acid, crystallises in lustrous, white needles melting at  $140^\circ$ , and is slightly soluble in hot water.

*Parethoxyphenylfumaramide*,



obtained by heating malic acid with paraphenetidine at  $180^\circ$ , or by heating *parethoxyphenylmalamic acid*, forms shining, yellowish leaves melting at  $214^\circ$ . It readily takes up bromine, giving *parethoxyphenylbromosuccinamide*,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , which forms whitish crystals melting at  $199^\circ$ . T. H. P.

**Ortho-substituted Alkylanilines.** By PAUL FRIEDLÄNDER (*Monatsh.*, 1898, 19, 627—646).—The author has found that all ortho-substituted dialkylanilines (not substituted in the para-position) do not react with nitrous acid or with aldehydes. The power of combining with diazo-compounds is also greatly diminished, but not completely lost. These bases, moreover, invariably boil at lower temperatures than the corresponding monalkyl derivatives, whereas other dialkylanilines boil at higher temperatures than the corresponding monomethyl compounds. The two diortho-substituted dialkylanilines examined also behaved similarly. *Ethylorthotoluidine* boils at  $214^\circ$  (corr.), and condenses with formaldehyde, producing *diethyldiamidodiorthotolylmethane*, which crystallises in yellowish needles, melts at  $96^\circ$ , and boils at about  $300^\circ$  under a pressure of 40 mm. *Ethylic iodide* converts it into the corresponding *tetrethyl* compound, which is a yellow oil boiling at  $235$ — $245^\circ$  under 26 mm. pressure. *Diethylorthotoluidine* does not react with formaldehyde. *Ethylorthophenetidine* is a colourless oil which boils at  $238^\circ$ , and readily reacts with formaldehyde and diazo-compounds. *Diethylorthophenetidine* boils at  $231$ — $233^\circ$ , and forms a *platinochloride* which crystallises in light yellow needles. It does not react with nitrous acid or formaldehyde, but forms a red azo-colouring matter with paranitrodiazobenzene. Monomethylorthonitraniline, which can be prepared by methylating orthonitraniline, yields a condensation product with formaldehyde. *Dimethylorthonitraniline* is best prepared by heating crude orthodinitrobenzene with dimethylamine. It is a reddish-yellow oil which decomposes when heated, and does not react with nitrous acid, aldehydes, or diazo-compounds; the *platinochloride* crystallises in short, yellow needles. *Orthamidobenzonitrile* melts, when pure, at  $50$ — $51^\circ$ , and its *acetyl* derivative at  $132.5^\circ$ . *Ethylorthamidobenzonitrile* crystallises in long, colourless needles melting at  $32^\circ$ , and yields azo-colouring matters in the usual manner; its *acetyl* derivative is liquid, and boils at  $268$ — $275^\circ$ . *Diethylorthamidobenzonitrile* boils



at 165—175° under 95 mm. pressure, and does not react with nitrous acid or diazo-compounds. Dimethylortho-chloraniline, when pure, does not react with nitrous acid as stated by Heidelberg (Abstr., 1887, 474); it boils at 206°, whilst the monomethyl compound boils at 214°.

DERIVATIVES OF METAXYLIDINE [ $\text{Me}_2:\text{NH}_2 = 1:3:2$ ]. [With PH. BRAND.]—The *benzoyl* derivative crystallises in silky needles melting at 164°. Metaxylidine very readily reacts with formaldehyde, yielding *diamidodixylylmethane*,  $\text{CH}_2(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NH}_2)_2$ , which crystallises in white needles melting at 126°, and forms a *diacetate* crystallising in plates which do not melt below 280°. It also reacts with *para*-nitrobenzaldehyde, forming *paranitrodiamidophenyldixylylmethane*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NH}_2)_2$ , which melts at 136°, and yields a *diacetyl* compound crystallising in colourless needles. Metaxylidine readily forms a dark red azo-colouring matter with *para*-nitrodiazobenzene. *Methylmetaxylidine*, formed by the action of methylic iodide on the base, is a colourless oil boiling at 206—207°; the *hydrochloride* is readily soluble, and the *platinochloride* forms yellow needles. Its *acetyl* derivative crystallises in large tablets and melts at 94—95°; all attempts to hydrolyse this compound were unsuccessful, as it resists the action of boiling 80 per cent. sulphuric acid, or of alcoholic potash at 220°. Condensation products with aldehydes or azo-colouring matters could not be obtained from the base, and this diortho-substituted monomethylaniline therefore behaves in this respect like a monortho-substituted dimethylaniline. *Dimethylmetaxylidine* boils at 195—196°, and smells like camphor; it does not react with nitrous acid, aldehydes, or diazo-compounds. *Ethylmetaxylidine* is a colourless oil boiling at 217—218°, and closely resembles the corresponding methyl compound. The *diethyl* derivative boils at 220—221°, and forms a *platinochloride* crystallising in small, yellow needles.

A. H.

The Quinquevalent Asymmetric Nitrogen Atom. I. Occupation of Space. II. Inactive Isomerides. By EDGAR WEDEKIND (*Ber.*, 1899, 32, 511—516, 517—529).—The author has endeavoured to ascertain the capacity of nitrogen compounds for yielding derivatives in which the nitrogen is quinquevalent. The possible formation of inactive isomerides has also been kept in view, and the question of optical activity arising from asymmetry of nitrogen has been considered.

When diphenylmethylamine is heated with methylic iodide (1 mol.) during 5—6 hours at 150°, no substituted ammonium iodide is produced, although a mixture of dimethylaniline and methylic iodide yields 93 per cent. after an interval of 53 hours without application of heat; dimethylaniline yields only 3 per cent. of the ammonium iodide when treated with cold normal propylic iodide, and 0.9 per cent. with isopropylic iodide, whilst allylic iodide gives 88.5 per cent. Methylic iodide has no action on cold di-isopropylaniline, with which action does not begin until a temperature of 100° is reached.

Isopropylic iodide yields 4 per cent. of ammonium salt when heated with tribenzylamine at 100° during 6 hours, whilst the normal iodide has no action. This peculiarity must depend less on the pentad nature of

nitrogen than on the influence of the benzylic radicle, because dimethylaniline under similar conditions combines less readily with isopropyl iodide than with the normal salt. In this connection, it is noteworthy that when benzylic chloride acts on allylaniline, a considerable amount of dibenzylaniline is produced; the latter is also formed when allylic bromide acts on benzylaniline.

Attempts to produce the same system by introducing the radicles in different order have been shown to meet with various degrees of success (compare Menshutkin, Abstr., 1895, ii, 385). It should be possible to prepare phenylbenzylethylallylammonium iodide by the three following methods. 1. Action of benzylic iodide on ethylallylaniline. 2. Action of allylic iodide on benzylethylaniline. 3. Action of ethylic iodide on benzylallylaniline. In practice, however, the first only of these methods was successful, whilst the third produced no result whatever.

Acetomethylanilide does not combine with methylic iodide when heated at  $150^{\circ}$  during 5 hours, but yields a viscous oil at  $220-250^{\circ}$ ; this illustrates the influence exerted by negative radicles on the ease with which substituted ammonium salts are produced. Compounds more strongly basic in character do not display this feature to the same extent, *ethylic piperidinoacetate benzyl-bromide* or *-iodide* being formed when ethylic bromacetate or iodacetate acts on benzylpiperidine; the iodide,  $C_5H_{10}NI(CH_2Ph) \cdot CH_2 \cdot COOEt$ , crystallises in monoclinic plates or prisms, and melts at  $193-195^{\circ}$ . Methylic bromacetate and iodacetate combine very readily with benzylpiperidine, which also yields an ammonium salt with methylic bromomalonate; the products in each case, excepting the last, can be prepared by the inverse process, namely, addition of benzylic iodide or bromide to the ethereal piperidinoacetate,  $C_5H_{10}N \cdot CH_2 \cdot COOR$ . These ammonium iodides lose a portion of their halogen on treatment with a boiling solution of barium hydroxide, the ethereal carboxylate being simultaneously hydrolysed.

In certain circumstances, therefore, two affinities of quinquevalent nitrogen can be satisfied by negative radicles. This has been shown by Lachmann, who prepared triethylamine dibromide,  $NEt_3Br_2$ , but failed to obtain nitrogen pentethyl,  $NEt_5$ , from it by the action of zinc ethyl; moreover, molecular silver has no action on phenyltrimethylammonium bromide.

*Phenylparanitrobenzyltrimethylammonium chloride*,



obtained from paranitrobenzylic chloride and dimethylaniline, crystallises from a mixture of ether and alcohol in colourless leaflets, and melts at  $118-120^{\circ}$ .

It has been noticed by Le Bel that trimethylisobutylammonium platinochloride occurs in two forms which differ crystallographically from one another, and observations of a similar character have been made by Collie and Schryver, Menshutkin, and Miss Evans; the author finds that phenylbenzylmethylallylammonium iodide, when prepared by the addition of allylic or benzylic iodide to benzylmethylaniline or methylallylaniline respectively, differs in physical properties from the salt obtained by the action of methylic iodide on benzylallylaniline.

*a*-Phenylbenzylmethylallyl ammonium iodide,  $\text{CH}_2\text{Ph}\cdot\text{NMe}(\text{C}_3\text{H}_5)\text{PhI}$ , prepared by agitating benzylmethylaniline (20 grams) with allylic iodide (17 grams), and filtering the crystalline product after an interval of 24 hours, crystallises from 50 per cent. alcohol, and melts and decomposes at  $140\text{--}142^\circ$ ; it is identical with the product from methylallylaniline and benzylic iodide. The salt crystallises in the rhombic system [ $a:b:c=0.8915:1:0.6637$ ]. The  $\beta$ -modification, obtained by the action of methylic iodide (13.6 grams) on benzylallylaniline (17.6 grams) during 3—4 days, crystallises from 50 per cent. alcohol in beautiful prisms belonging to the rhombic system [ $a:b:c=0.6779:1:1.0392$ ], and melts at  $158\text{--}159^\circ$ . The specific gravity is higher than that of the isomeride.

*Benzylallylaniline*,  $\text{C}_3\text{H}_5\cdot\text{NPh}\cdot\text{CH}_2\text{Ph}$ , prepared from allylaniline and benzylic chloride, boils at  $215\text{--}225^\circ$  under 42 mm. pressure; the *hydrochloride* crystallises from alcohol in colourless leaflets and melts at  $220\text{--}221^\circ$ . The *methylallylaniline*,  $\text{NMePh}\cdot\text{C}_3\text{H}_5$ , obtained from allylic bromide and methylaniline, boils at  $213^\circ$  under a pressure of 755 mm.

The author has examined numerous ammonium iodides, which will be described in a subsequent communication; several cases of isomerism similar to that exhibited by the phenylbenzylmethylallyl ammonium iodides have been observed.

M. O. F.

**Action of Formaldehyde on Orthodiamines II.** By OTTO FISCHER (*Ber.*, 1899, 32, 245—247).—Fischer and Wreszinski (*Abstr.*, 1892, 1496) have previously shown that, by the action of formaldehyde on orthodiamines in acid solution, methylated imidazoles are produced, whilst in neutral solution more complex bases are formed by the condensation of two molecules of the diamine with four molecules of formaldehyde. The base from orthophenylenediamine has the composition

$\text{C}_{16}\text{H}_{16}\text{N}_4$ , and the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{CH}_2 \diagup \\ \diagup \text{N} \diagdown \\ \diagdown \text{CH}_2 \diagup \end{array} \text{C}_6\text{H}_4$  is

now assigned to it. The salts gradually undergo decomposition when exposed to the air, yielding formaldehyde, and a similar decomposition takes place on boiling with dilute sulphuric acid; in the latter case, the original diamine can be detected amongst the products. In accordance with the formula assigned to it, the base is very stable towards reducing agents, and when dissolved in alcohol or amyl alcohol it is not acted on either by sodium or by potassium; towards alkyl iodides, it behaves as a tertiary base, and combines directly with two molecular proportions of methylic or ethylic iodide. A similar formula has recently been assigned by Bischoff (*this vol.*, i, 279) to the analogous base prepared from formaldehyde and ethylenediamine.

T. M. L.

**Phenylparatolylformamidine and the Transformation of Imidoethers.** By HENRY L. WHEELER and T. B. JOHNSON (*Ber.*, 1899, 32, 35—41. Compare *Abstr.*, 1897, i, 465).—After examining Walther's results experimentally (*Abstr.*, 1898, i, 519; 1897, i, 242), the authors arrived at the following conclusions. "Up to the present, only one phenylparatolylformamidine is known. It melts at  $86^\circ$  when

pure. This amidine is the only mixed amidine that is formed in all four of Zwingenberger and Walther's experiments, but its detection is rendered difficult by the presence of other amidines; these are diphenylamidine and diparatolylamidine. The supposed phenylparatolylamidine melting at  $132^{\circ}$  is nothing but impure diparatolylamidine, that melting at  $120^{\circ}$  is impure diphenylamidine, whilst those melting at  $102^{\circ}$  and  $98^{\circ}$  are mixtures of phenylparatolylamidine, diphenylamidine, and diparatolylamidine in varying proportions."

When the silver derivative of formanilide,  $\text{NPh}\cdot\text{CH}\cdot\text{OAg}$ , is heated with excess of ethylic iodide at  $100^{\circ}$  for 6 hours, the product is not phenylformimidoethylic ether,  $\text{NPh}\cdot\text{CH}\cdot\text{OEt}$ , but formethylanilide  $\text{NEtPh}\cdot\text{CHO}$ . In a similar manner, benzimido-ethylic ether,  $\text{NH}\cdot\text{CPh}\cdot\text{OEt}$ , yields benzethylamide,  $\text{NH}\cdot\text{Et}\cdot\text{CPhO}$ . C. F. B.

**A New Class of Dyes, the Diamidodiphenylbenzenylamidines.** By EMILIO NOELTING and KUNTZ (*Chem. Centr.*, 1898, ii, 1049; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 395—397).—Diphenylbenzenylamidine,  $\text{NPh}\cdot\text{CPh}\cdot\text{NPh}$ , and its methyl derivative are white, and have no colouring properties, but when an amido- or a dimethylamido-group is introduced into these compounds, faint yellow dyes are formed, and by the introduction of two such groups diamidodiphenylbenzenylamidines are obtained which dye wool, silk, and cotton mordanted with tannin, an intense yellow. The latter dyes are prepared by the action of dimethylparamidobenzomethylanilide on aniline, paraphenylenediamine, or dimethylparaphenylenediamine in presence of phosphorus oxychloride. Diphenylbenzenylmethylamidine must therefore be regarded as a chromogen, since it yields dyes when auxochromic groups are introduced into it.

E. W. W.

**Amidines (Iminoamines).** By FERNAND MUTTELET (*Ann. Chim. Phys.*, 1898, [vii], 14, 391—432).—A study of the reaction between aromatic mono-substituted orthodiamines and benzoic chloride and its derivatives (*Abstr.*, 1898, i, 412). When 2-amidodiphenylamine is heated at  $215^{\circ}$  with excess of 4-nitrobenzoic chloride, the inner *anhydride*,  $\text{C}_6\text{H}_4\langle\text{NPh}\rangle\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , is produced; it crystallises from alcohol in needles melting at  $174^{\circ}$ . The *anhydride* obtained in a similar manner from 2-amidophenylparatoluidine, crystallises in yellow needles melting at  $174$ — $175^{\circ}$ .

The *anhydride*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\langle\text{NPh}\rangle\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , obtained from 4-nitro-2-amidodiphenylamine and 4-nitrobenzoic chloride, crystallises from benzene in yellow, lamellated crystals melting at  $205^{\circ}$ .

The *anhydride* containing the paratolyl group in the place of phenyl in the preceding compound, crystallises from benzene in yellow scales and melts at  $250$ — $251^{\circ}$ .

These nitro-anhydrides, on reduction, yield amido-amidines (compare *loc. cit.*); the following are described for the first time. The compound  $\text{C}_6\text{H}_4\langle\text{NPh}\rangle\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  melts at  $198$ — $199^{\circ}$ ; its *sulphate* crystallises with  $2\text{H}_2\text{O}$ , and its *hydrochloride* with  $1\frac{1}{2}\text{H}_2\text{O}$ . The corre-

sponding *paratolyl* compound melts at 187—188°; its *sulphate* and *hydrochloride* are described. The compound  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{NPh} \\ \diagup \quad \diagdown \\ \text{---} \quad \text{N} \end{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NH}_2$  crystallises in needles and melts at 270—272°, its *sulphate* crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$ ; the *paratolyl* compound melts at 252—253°; its *sulphate* crystallises with  $4\text{H}_2\text{O}$ .

The amidines containing one amido-group, just described, yield azo-derivatives when diazotised and combined with  $\beta$ -naphthol; the amidines containing two amido-groups give rise to tetrazo-compounds. The azo-dyes obtained from the monamidoamidines and naphthol- and amidonaphthol-sulphonic acids are incapable of dyeing unmordanted cotton, whereas the tetrazo-compounds from the diamidoamidines are substantive colours comparable with those of commerce.

G. T. M.

**Hydrolysis of Mixed Azo-compounds.** By EUGEN BAMBERGER (*Chem. Centr.*, 1898, ii, 1050; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 384—385).—The relationship of aliphylazonitroparaffins to phenylhydrazine is shown by their decomposition into nitrous acid and  $\beta$ -acylphenylhydrazides by the action of alkalis. Phenylazonitropropane yields propionophenylhydrazide,  $\text{EtCO} \cdot \text{N}_2\text{H}_2\text{Ph}$ ; phenylazonitroethane yields acetophenylhydrazide, and phenylazonitropentane gives valerophenylhydrazide. In a similar manner, oxyformazyl is formed from nitroformazyl, but cannot be isolated, as it changes into

the betaine of diphenyloxytetrazolium hydroxide,  $\text{N} \begin{smallmatrix} \text{NPh} \cdot \text{NPh} \\ \diagup \quad \diagdown \\ \text{C} = \text{N} \end{smallmatrix} \text{O}^-$ ,

which crystallises in white needles, explodes at 174°, and yields insoluble salts with potassium permanganate, potassium dichromate, picric acid, and gold and platinum chlorides.

E. W. W.

**Ethylic [*b*-Aniline-azo]-acetoacetate (Ethylic Acetylglyoxylate- $\alpha$ -phenylhydrazone, Ethylic Benzeneazoacetoacetate).** By CARL BÜLOW (*Ber.*, 1899, 32, 197—210. Compare this vol., i, 271).—The compound formed when the sodium compound of isodiazobenzene reacts with ethylic acetoacetate in slightly alkaline solution, is identical with that obtained by Kjellin from this ethylic salt and benzene-diazonium chloride, and is evidently *ethylic benzeneazoacetoacetate*,  $\text{Ph} \cdot \text{N}_2 \cdot \text{CHAc} \cdot \text{COOEt}$ ; it crystallises in broad, sulphur-yellow needles, melts at 73—74°, and dissolves in 1 per cent. sodium hydroxide solution with an intense red coloration, the solution being decomposed by carbonic anhydride, with re-formation of the ethylic salt. It would therefore seem that the CH-group, in conjunction with the chromophore group  $\text{N}:\text{N}$ , acts as an auxochrome.

*Sodium benzeneazoacetoacetate*, prepared by adding sodium hydroxide solution to an alcoholic solution of the ethylic salt, forms yellowish-white crystals, melts at 195°, and, on further treatment with sodium hydroxide, forms a disodium compound, which is, however, stable only in dilute alkaline solution; the sodium salt is not decomposed by carbonic anhydride. The phenylhydrazone of the acid is best prepared by adding an alcoholic solution of phenylhydrazine to an aqueous solution of the sodium salt; it can be precipitated, not only

by the addition of acetic acid, but also by means of mineral acids, without being converted into 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone, which is formed only on boiling the solution. The *methylamide*, which is prepared by adding methylamine to an alcoholic solution of the ethylic salt, crystallises in yellow needles melting at 150.5°, and on nitration passes into paranitrobenzeneazoacetomethylamide melting at 190°.

*Ethylic benzeneazoacetate-β-phenylhydrazone* is very unstable, readily passing into the pyrazolone by the elimination of alcohol; it forms orange needles and melts at 108–109°.

On nitration, ethylic benzeneazoacetate gives the same nitro-compound as that prepared from the isodiazo-derivative of paranitraniline and ethylic acetoacetate; this, on treatment with phenylhydrazine, passes into 1-phenyl-3-methyl-4-benzeneazo-5-pyrazolone, melting at 198°; the true *β-phenylhydrazone*, prepared from the sodium salt of the acid by the addition of phenylhydrazine, is an orange, crystalline powder which readily passes into the pyrazolone on heating with acids.

J. F. T.

**Unsymmetrical Phenylhydrazine Derivatives. V. Ethylic Phenylhydrazidoformate.** By HANS RUPE and HANS LABHARDT (*Ber.*, 1899, 32, 10–17. Compare Abstr., 1896, i, 429).—*Ethylic acetophenylhydrazidoformate*,  $\text{NHAc} \cdot \text{NPh} \cdot \text{COOEt}$ , is obtained by boiling acetophenylhydrazide (1 mol.) with ethylic chloroformate (1 mol.) in benzene solution; it melts at 72–73°. When it is distilled, it loses

alcohol and yields 1-phenyl-4-methyl-3-oxybiazalone,  $\begin{matrix} \text{NPh} \cdot \text{CO} \\ | \\ \text{N} = \text{CMe} \end{matrix} > \text{O}$  (Freund and Goldschmidt, Abstr., 1888, 686, 1187); when boiled with 10 per cent. sulphuric acid and enough alcohol to effect solution, it is converted into ethylic phenylhydrazidoformate,  $\text{NH}_2 \cdot \text{NPh} \cdot \text{COOEt}$  (*loc. cit.*), which boils at 157° under a pressure of 15 mm., has basic properties, and is unstable in the air; the *orthonitrobenzylidene* derivative is yellow, and melts at 85–86°. Ethylic phenylsemicarbazide-carboxylate,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh} \cdot \text{COOEt}$  (*loc. cit.*), is better obtained by boiling phenylsemicarbazide (1 mol.) with ethylic chloroformate (2 mols.) in benzene solution; its melting point is now given as 172°;

from it, 1-phenylurazole,  $\begin{matrix} \text{NPh} \cdot \text{CO} \\ | \\ \text{NH} - \text{CO} \end{matrix} > \text{NH}$ , can be obtained by heating with alkalis or alkali carbonates. On dissolving it in dilute hydrochloric acid and adding sodium nitrite, a reddish-yellow *nitroso*-derivative, melting and decomposing at about 75°, is obtained. In cooled ethereal solution, ethylic phenylhydrazidoformate (2 mols.) reacts with ethylic chloroformate (1 mol.), forming *phenylhydrazine-α-β-dicarboxylate*,  $\text{COOEt} \cdot \text{NH} \cdot \text{NPh} \cdot \text{COOEt}$ , which melts at 58–60°, yields diphenylcarbamide when heated with aniline, and the above mentioned biazolone when fused with acetamide; it can also be obtained by boiling ethylic phenylcarbazinate,  $\text{COOEt} \cdot \text{NH} \cdot \text{NHPh}$ , with ethylic chloroformate in benzene solution. The tetrazine described previously (*loc. cit.*) is identical with compounds to which slightly different formulæ have been assigned by Pinner (Abstr., 1888, 1084) and Heller (Abstr., 1891, 1213).

C. F. B.

**Constitution of Phenylhydrazones.** By PAUL C. FREER (*Amer. Chem. J.*, 1899, 21, 14—64).—Phenylhydrazones are usually regarded as having the formula  $\text{CHRR}'\cdot\text{C}(\text{CR}'')_3\cdot\text{N}\cdot\text{NHPh}$ , but certain members of this class of substances appear to have a hydrazo-structure,  $\text{CRR}'\cdot\text{C}(\text{CR}'')_3\cdot\text{NH}\cdot\text{NHPh}$ ; the latter are readily oxidised to azo-compounds, whilst the true hydrazones do not undergo this change. The azo-compounds so obtained form perbromides; reduction with sodium amalgam reconverts both the azo-derivative and its perbromide into the original hydrazone compound. The true hydrazones are either not affected by benzoic chloride or, if acted on by this reagent, they yield only benzoyl derivatives; the hydrazo-compounds, treated in a similar manner, give rise to dibenzoyl derivatives, and when these are unstable dibenzophenylhydrazide is the final product. The result of adding hydrocyanic acid to a hydrazone will be the same whichever of the above formulæ is assumed to be correct, hence this reaction cannot be used to distinguish between the two classes of compounds; moreover, the property of forming an additive compound is not a general one.

Dibenzophenylhydrazide is obtained by the action of benzoic chloride on the hydrazones of acetone and acetophenone, and benzoic anhydride behaves in a similar manner; neither of these hydrazones can be benzoylated by the Schotten-Baumann method. Benzaldehyde and phthalic anhydride decompose acetonephenylhydrazone, yielding benzylidenephénylhydrazone and phthalylphenylhydrazones respectively.

1 : 4-Bromobenzeneazostyrene (compare Abstr., 1897, i, 342), prepared from acetophenonephenylhydrazone, crystallises from petroleum in reddish prisms and melts at  $48^\circ$ , exploding violently when further heated; it is reconverted into the hydrazone by sodium amalgam. The perbromide resembles the corresponding acetone derivative, but is probably a mixture of two substances.

1 : 4-Benzobromophenylhydrazide,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NHBz}$ , which is formed by the action of bromine on an ethereal solution of benzophenylhydrazide, crystallises in lustrous, white leaflets melting at  $156^\circ$ .

1 : 4-Benzoylazobromobenzene,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\cdot\text{COPh}$ , obtained by oxidising the preceding compound with mercuric oxide suspended in dry ether and concentrating the filtrate in a vacuum, forms red plates melting at  $69^\circ$ ; when pure, it is stable; on heating, it gives off nitrogen at  $133^\circ$  and benzoic acid at  $142^\circ$ ; on reduction with sodium amalgam, the hydrazide is regenerated. The perbromide,  $\text{C}_{13}\text{H}_9\text{N}_2\text{OBr}_5\text{Br}$ , formed on adding bromine to a chloroform solution of the azo-compound, crystallises in garnet-red prisms and melts and decomposes at  $123^\circ$ . Another perbromide,  $\text{C}_{13}\text{H}_9\text{N}_2\text{OBr}_4\text{Br}$ , is produced at the same time, and is also formed when the preceding compound is treated with cold alcohol; it is, moreover, the sole product when the reaction is performed in glacial acetic acid.

1 : 4-Acetobromophenylhydrazide, obtained in a similar manner to the benzoyl derivative, crystallises from alcohol in leaflets and melts at  $161^\circ$ . When treated with concentrated hydrocyanic acid, it yields a hydrocyanide,  $\text{C}_{10}\text{H}_{12}\text{BrN}_3$ , crystallising in hard prisms, and melting at  $95\text{--}96^\circ$ ; when oxidised with mercuric oxide, the hydrazide is converted into a red oil which gives a yellow perbromide.

Pyruvic acid hydrazone does not behave like these hydrazo-compounds; it is not oxidised to an azo-compound on exposure to air, and on treatment with mercuric oxide it gives rise to a *substance* which is probably the acetophenylhydrazide of pyruvic acid hydrazone,  $C_{17}H_{18}N_4O_2$ , since it is hydrolysed by alkalis into acetophenylhydrazide and pyruvic acid phenylhydrazone. Benzylidenephénylhydrazone is also a true hydrazone, since it is not oxidised to an azo-compound. Some ketones and aldehydes appear to yield hydrazones belonging to both classes. Smith and Ransom (Abstr., 1894, i, 294) have already obtained two isomeric benzoinphenylhydrazones, and the author, by treating an ethereal solution of the  $\beta$ -compound with a small quantity of benzoic chloride, has now produced a third isomeride,  $\gamma$ -benzoinphenylhydrazone, which crystallises from alcohol in plates, and melts at  $162^\circ$ . Neither the  $\alpha$ - nor the  $\gamma$ -compound reacts with benzoic chloride at ordinary temperatures. The  $\beta$ -isomeride, when oxidised by nitrous anhydride (?), yields a *substance* the composition of which corresponds with that required by the formula  $C_{20}H_{16}N_6O_3$ ; it crystallises from alcohol in red needles decomposing at  $137^\circ$ . The  $\alpha$ -isomeride, when similarly treated, does not yield a red substance, and the  $\gamma$ -compound is not affected by the oxides of nitrogen.

It appears probable that the  $\beta$ -modification has the hydrazo-structure, but the exact constitution of the three isomerides has yet to be determined.

Preliminary experiments on Fischer's two ethylidenephénylhydrazones (Abstr., 1896, i, 361) seem to indicate that the  $\beta$ -variety (m. p.  $60^\circ$ ) is the hydrazo-compound, and that a third modification may exist which melts at  $80^\circ$ .

The compound, obtained by Hess from phenylhydrazine and bromacetophenone, when heated with glacial acetic acid or alcoholic hydrogen chloride, yields a *substance* having the composition  $C_{20}H_{18}N_2$ ; this crystallises in white, silky needles and melts at  $114^\circ$ — $115^\circ$ .

The compound,  $NHPh \cdot NH \cdot CH_2 \cdot CH \cdot N \cdot NHPh$ , produced by the action of chloroacetaldehyde hydrate and phenylhydrazine in alcoholic solution, forms colourless prisms and melts at  $94^\circ$ — $95^\circ$ ; when boiled with alcohol or benzene, it seems to undergo polymerisation; sodium amalgam reduces it readily, forming symmetrical *diphenylethylenehydrazine*,  $C_2H_4(NH \cdot NHPh)_2$ , which crystallises in white needles melting at  $100^\circ$ .

G. T. M.

**Salicylparaphenetidine and its Derivatives.** By GIOVANNI BOLEZZI (*Gazzetta*, 1898, 28, ii, 197—202).—Salicylparaphenetidine has been prepared by Scholvién by heating a mixture of paramidophenetoil and salicylic acid with phosphorus trichloride; by this method, a pure product cannot be obtained, owing to the separation of an oil. The author finds that by heating a mixture of salicylic acid and paraphenetidine sulphate, in molecular proportion, at  $210^\circ$ , the compound is obtained in a much cleaner form, and on crystallisation from dilute spirit, forms glistening laminæ, having a pearly lustre, and melting at  $142^\circ$ — $143^\circ$  instead of  $139.5^\circ$ . It is soluble in alcohol, ether, and acetic acid, but insoluble in water, and yields



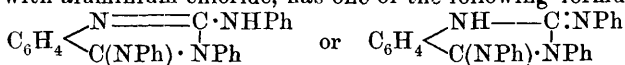
an *acetyl* derivative,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OAc}$ , which forms white, silky needles melting at  $132^\circ$ , and is soluble in alcohol or acetic acid. The *benzoyl* derivative,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$ , crystallises in silky needles, melts at  $136\text{--}137^\circ$ , and is insoluble in water, but soluble in alcohol, ether, and acetic acid. T. H. P.

**Constitution of Salts of Imidoethers and other Carbimide Derivatives.** By JULIUS STIEGLITZ (*Amer. Chem. J.*, 1899, 21, 101—111).—This is a theoretical paper, bearing on the practical results described in the following abstract, and also on work not yet published; it deals with the constitution of the salts of carbimide bases. When carbimide derivatives combine with acids, the products are usually considered to contain quinquivalent nitrogen in the group  $\text{--C}^{\text{v}}\text{:NRHCl}$ , but it is already admitted that sometimes the addition occurs at the double linking, as in the case of isocyanates, and the additive products of hydrocyanic acid and fulminic acid. It is assumed that the salts of the imidoethers,  $\text{OR} \cdot \text{RC}^{\text{v}}\text{:NR}$ , the amidines  $\text{NHR} \cdot \text{RC}^{\text{v}}\text{:NR}$ , the pyridines, and quinolines contain quinquivalent nitrogen doubly linked to carbon,  $>\text{C}^{\text{v}}\text{:NRHCl}$ ; the alternative constitution,  $>\text{CCl} \cdot \text{NHR}$ , for these derivatives has not been considered. The hydrobromide of 1:2-chloromethenylamidophenol and the hydrochloride of the corresponding bromo-compound are identical, and they must have the formula  $\text{CClBr} \cdot \text{C}_6\text{H}_4 \cdot \text{N}^{\text{v}}\text{H} \cdot \text{O}$ . The hydroxides from the alkylquinolinium salts are now considered to contain the group  $\text{--N}^{\text{v}}\text{R} \cdot \text{CH}(\text{OH})\text{--}$  and not  $\text{--N}^{\text{v}}\text{R}(\text{OH})\text{:CH--}$ , and it seems quite likely that their salts may also have a constitution corresponding with the former of these formulæ. G. T. M.

**Hydrochlorides of Carbophenylimido-derivatives.** By HERBERT N. MCCOY (*Amer. Chem. J.*, 1899, 21, 111—167. Compare preceding abstract).—3:5-Dibromocarboxylamidophenol, produced by the action of potassium hypobromite on salicylamide, crystallises in needles and melts at  $250^\circ$ ; it is not identical with the dibromocarbonylamidophenol (m. p.  $243\text{--}245^\circ$ ) obtained by Jakoby by the direct bromination of carbonylamidophenol. Both isomerides are readily reduced to the latter substance by sodium amalgam. The 3:5-compound may be synthesised from 3:5-dibromosalicylamide. The *alkali* salts of both isomerides are described. 1:2-Carbonylamidophenol is best prepared by Bender's method from so-called ethylic 1:2-amidophenylic carbonate; the latter substance is insoluble in acids but dissolves readily in alkalis, and is really a hydroxy-compound obtained by intramolecular rearrangement from the initially formed amidocarbonate,  $\text{NH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{COOEt}$ , and having a constitution corresponding with one or other of the following formulæ:  $\text{C}_6\text{H}_4 \cdot \text{N}^{\text{v}}\text{H} \cdot \text{O} \cdot \text{C}(\text{OH}) \cdot \text{OEt}$  or  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{COOEt}$ . An excellent yield of 1:2-chloromethenylamidophenol is obtained by passing dry chlorine into a cold solution of 1:2-thiocarbamidophenol in chloro-

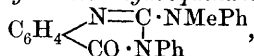
form, and the 1:2-bromomethenylamidophenol,  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{O} \end{smallmatrix} \text{CBr}$ , obtained by the substitution of bromine for chlorine in this reaction, forms white crystals melting at  $27^\circ$ . These substances are not produced by the action of the phosphorus halogen compounds on 1:2-carbonylamidophenol. 1:2-Chloromethenylamidophenol hydrochloride (1:2-dichlorocarbonylamidophenol),  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} \text{CCl}_2$ , prepared by passing hydrogen chloride into a solution of the chloromethenyl compound in petroleum, forms white crystals melting at  $57-58^\circ$ ; it is very unstable, and can only be kept in an atmosphere of hydrogen chloride. The nitrate forms white crystals and the platinochloride is orange coloured; both salts are decomposed by water. The hydrobromide (1:2-chlorobromocarbonylamidophenol),  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} \text{CClBr}$ , is more stable than the hydrochloride, and decomposes at  $155^\circ$ ; it is prepared either by adding hydrogen bromide to chloromethenylamidophenol, or hydrogen chloride to the bromo-derivative; water decomposes it into the chloro-derivative and hydrogen bromide. 1:2-Bromomethenylamidophenol hydrobromide (1:2-dibromocarbonylamidophenol) melts at  $163^\circ$ , and is also decomposed by water.

The compound,  $C_{26}H_{20}N_4$ , obtained by condensing carbodiphenylimide with aluminium chloride, has one of the following formulæ:



(Abstr., 1897, i, 422, 490). The latter is now shown to be more probable. The compound, on hydrolysis, yields a substance,  $C_{20}H_{15}N_3O$ , which is either  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{CO \cdot NPh} \end{smallmatrix} \text{C(NPh) \cdot NPh}$  or  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{CO \cdot NPh} \end{smallmatrix} \text{C(NPh) \cdot NPh}$ . This when heated with methylic iodide for 9 hours at  $100^\circ$ , yields a methyl derivative which crystallises in colourless needles melting at  $174^\circ$ . The latter compound, on hydrolysis, yields aniline and 1'-methyl-2':4'-diketo-3'-phenyltetrahydroquinazoline, which melts at  $223^\circ$ , and is identical with the product obtained by methylating 2':4'-diketo-3'-phenyltetrahydroquinazoline. Fortmann gives  $233^\circ$  as the melting point for this compound.

2'-Methylanilido-3'-phenyl-4-ketodihydroquinazoline,



the isomeride of the above methyl derivative, obtained by heating 2'-chloro-3'-phenyl-4-ketodihydroquinazoline with methylaniline at  $180^\circ$  for 2 hours, crystallises from dilute methylic alcohol or from ether and petroleum in needles melting at  $123^\circ$ .

The two modifications of 2':4'-diphenylimido-3'-phenyltetrahydroquinazoline behave differently towards phenylcarbimide; the  $\alpha$ -form yields a phenylcarbamide derivative, whereas the  $\beta$ -form does not.

2'-Methylthio-3'-phenyl-4'-ketodihydroquinazoline,  $C_6H_4 \begin{smallmatrix} \text{CO \cdot NPh} \\ \text{N : C \cdot SMe} \end{smallmatrix}$ , obtained on treating 2'-thio-3'-phenyl-4'-ketotetrahydroquinazoline with

methylic iodide and alcoholic potash, forms long needles melting at  $125^{\circ}$ . Its isomeride, the nitrogen ether, melts at  $288-289^{\circ}$ .

2'-Methoxy-3'-phenyl-4'-ketodihydroquinazoline,  $\text{C}_6\text{H}_4 \begin{matrix} \swarrow \text{N}=\text{C}\cdot\text{OMe} \\ \searrow \text{CO}\cdot\text{NPh} \end{matrix}$ ,

from 2'-chloro-3'-phenyl-4'-ketodihydroquinazoline and sodium methoxide, crystallises in rhombohedra and melts at  $134^{\circ}$ . G. T. M.

**Mercurio-methacetin** [-paracetamidophenylic methylic ether] and **Mercurio- $\alpha$ -acenaphthalide**. By L. PRUSSIA (*Gazzetta*, 1898, 28, ii, 122-129).—*Mercurio-methacetin*,  $\text{Hg}(\text{NAc}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , separates in tufts of slender, colourless needles melting at  $191.5^{\circ}$ , on filtering and cooling a hot solution of methacetin and mercuric chloride to which sodium carbonate has been added. It is decomposed by cold chloroform or by hot ethylic or methylic alcohol, benzene, or water; its composition was proved by treating it with sodium thiosulphate, potassium iodide, and ammonium bromide; in each case, methacetin and alkali are liberated.

*Mercurio- $\alpha$ -acenaphthalide*,  $\text{Hg}(\text{NAc}\cdot\text{C}_{10}\text{H}_7)_2$ , prepared by a method analogous to that described above, crystallises in microscopic laminae, apparently rhombic, which soften at  $199^{\circ}$  and melt at  $202^{\circ}$ . It is soluble in boiling water, but alcohol decomposes it; it is insoluble in ether. T. H. P.

**Organo-mercuric Compounds of Diphenylamine**. By L. PRUSSIA (*Gazzetta*, 1898, 28, ii, 129-132. Compare Abstr., 1897, i, 337).—Diphenylamine reacts with mercuric salts giving compounds containing mercury, one atom combined directly with basic nitrogen and another with the aromatic nuclei. All these compounds contain a bivalent radicle of the constitution  $\text{Hg} \begin{matrix} \swarrow \text{C}_6\text{H}_4\cdot\text{NHPh} \\ \searrow \text{C}_6\text{H}_4\cdot\text{NHPh} \end{matrix} \text{Hg}$ , which the author terms paramercuriodiphenylenediphenylmercuriodiammonium. The *hydroxide* of this base,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHPh}\cdot\text{OH})_2\text{Hg}$ , formed by treating the corresponding acetate with strong caustic potash solution, is a white, granular, amorphous substance which is almost insoluble in all the ordinary solvents, and its aqueous and alcoholic solutions have an alkaline reaction. It decomposes at above  $200^{\circ}$  without melting. The *acetate*,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHPh}\cdot\text{OAc})_2\text{Hg}$ , which separates on mixing alcoholic solutions of mercuric acetate and diphenylamine, crystallises from boiling alcohol in glistening, colourless laminae melting at  $178^{\circ}$ ; it is insoluble in water, but fairly soluble in boiling ethylic alcohol, or in benzene. The *chloride*,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHPhCl})_2\text{Hg}$ , prepared by mixing alcoholic solutions of the acetate and calcium chloride, forms a microscopic, colourless, nodular mass which softens at  $232^{\circ}$  and decomposes at above  $240^{\circ}$  without melting; it is sparingly soluble in methylic and ethylic alcohol, chloroform, benzene, and ether, and is insoluble in water. Sodium thiosulphate converts the hydroxide into *paramercuriodiphenylamine*,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{NHPh})_2$ , which separates from boiling benzene in rose-coloured tufts and melts at  $182.5^{\circ}$ .

T. H. P.

**Organo-mercuric Compounds of Diphenylmethylaniline**. By G. GARBARINI (*Gazzetta*, 1898, 28, ii, 132-134. Compare previous abstract).—Diphenylmethylaniline, with mercury salts, yields com-

pounds analogous to those formed by diphenylamine. These compounds contain the bivalent radicle,  $\text{Hg} \begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{NMePh} \\ \text{C}_6\text{H}_4 \cdot \text{NMePh} \end{smallmatrix} \text{Hg}$ , which the author terms paramercuriodiphenylenediphenyldimethylmercuriodiammonium.

The *hydroxide* of this base,  $\text{Hg}(\text{C}_6\text{H}_4 \cdot \text{NMePh} \cdot \text{OH})_2\text{Hg}$ , formed by acting on the corresponding acetate with caustic potash, is a white, amorphous mass, insoluble in the ordinary solvents. The *acetate*,  $\text{Hg}(\text{C}_6\text{H}_4 \cdot \text{NMePh} \cdot \text{OAc})_2\text{Hg}$ , prepared by mixing alcoholic solutions of diphenylmethylamine and mercuric acetate, crystallises from boiling alcohol in colourless needles melting at  $128^\circ$ . It is insoluble in water and benzene, and only slightly soluble in methylic or ethylic alcohol. On treating an aqueous solution of the hydroxide with sodium thiosulphate solution, paramercuriodiphenylmethylamine is deposited, and crystallises from a mixture of benzene and light petroleum in colourless laminae melting at  $138\text{--}139^\circ$ . T. H. P.

**Antimonylphenolic Compounds.** By HENRI CAUSSE (*Ann. Chim. Phys.*, 1898, [vii], 14, 526—564. Compare Abstr., 1892, 1078; 1898, i, 470).—*Antimonylcatechol acetate*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Sb} \cdot \text{OAc}$ ,

is obtained by the action of acetic anhydride on a solution of the hydroxide in glacial acetic acid in the presence of a trace of acetic chloride. The group  $\text{Sb} \cdot \text{OH}$  appears to be linked to both oxygen atoms of the catechol molecule, for when acetaldehyde is added to a solution of this phenol containing a halogen salt of antimony, no acetal compound is produced. Antimonylpyrogallol hydroxide is obtained by the action of pyrogallol on a solution of antimony oxide in tartaric acid (Abstr., 1893, i, 75). The *chloride*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{SbCl}$ ,

is best obtained by the action of antimony chloride on pyrogallol in methylic alcohol solution; the *bromide* is produced in a similar manner; it crystallises from dilute hydrobromic acid; the *iodide* is readily decomposed by water into a mixture of hydroxide and basic iodide; the *fluoride* is easily obtained by mixing solutions of antimony fluoride and pyrogallol, and crystallises from dilute hydrofluoric acid. These four salts form colourless crystals, closely resembling each other in physical and chemical properties. The *oxalate* is produced by adding a strong solution of potassium hydrogen oxalate to a solution of the chloride in dilute hydrochloric acid.

The *hydroxide*,  $\text{COOMe} \cdot \text{C}_6\text{H}_2(\text{OH}) \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Sb} \cdot \text{OH}$ , produced by mixing alcoholic solutions of methylic gallate and antimony chloride, separates as a white, crystalline powder which is freed from antimony chloride by washing with alcohol, and from antimonylphenolic chloride by treatment with hot water. Hydrochloric acid converts it into the *chloride*. The corresponding hydroxide from gallic acid has long been known; the *chloride*,  $\text{COOH} \cdot \text{C}_6\text{H}_4(\text{OH}) \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{SbCl}$ , the *bromide*, and the *potassium* salt,  $\text{COOK} \cdot \text{C}_6\text{H}_4(\text{OH}) \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Sb} \cdot \text{OH}$ , are now described for the first time. Catechol may be separated from

its isomerides by the addition of antimony fluoride to an aqueous solution of the three compounds when antimonycatechol fluoride is precipitated; the filtrate is treated with acetaldehyde, which removes resorcinol in the form of its acetal; the quinol in the final mother liquor is oxidised to insoluble quinhydrone by the addition of iodic acid.

G. T. M.

**Synthesis of Hydroxyaldehydes of the Benzene Series.** By LUDWIG GATTERMANN and M. KÖBNER (*Ber.*, 1899, 32, 278—283).—The authors find that the presence of aluminium chloride is not necessary, as was formerly thought (Gattermann and Berchemann, *Abstr.*, 1898, i, 561), for the preparation of hydroxy-aldehydes by the interaction of phenols with hydrogen cyanide, in presence of hydrogen chloride; zinc chloride, in most cases, produces the same result, whilst in a few instances, notably with resorcinol, orcinol, and phloroglucinol, no condensing agent at all is necessary. When either of the new modifications is adopted, ether can be employed as the solvent instead of benzene, as was formerly necessary; the method is thus rendered more suitable for the treatment of polyatomic phenols, which are sparingly soluble in benzene. The yield in most cases is nearly quantitative.

The crystalline *imide-hydrochloride*,  $C_6H_3(OH)_2 \cdot CH:NH, HCl$ , which separates initially (compare Gattermann, *Abstr.*, 1898, i, 476) in the preparation of 1:3:4-dihydroxybenzaldehyde from resorcinol by the above method, dissolves unchanged in cold water, but is decomposed by warm, giving rise to ammonium chloride and the corresponding aldehyde.

The *imide-hydrochloride* derived from phloroglucinol is, however, not decomposed by hot water, and is converted by dilute sulphuric acid into the corresponding *sulphate*,  $[C_6H_2(OH)_3 \cdot CH:NH]_2 \cdot H_2SO_4$ , which dissolves only sparingly in water; when the hydrochloride is boiled with dilute sulphuric acid, it is converted into 1:3:5:2-*trihydroxybenzaldehyde*. This crystallises from water in colourless needles containing  $2H_2O$ , softens when heated at  $105^\circ$ , and melts at no definite temperature; the aqueous solution of the aldehyde has a bitter taste, and produces, with ferric chloride, a wine-red coloration which remains unchanged on adding caustic soda.

The *imide-hydrochloride*,  $C_7H_8NClO_3$ , obtained from pyrogallol, is easily soluble in cold water, but separates from the aqueous solution, on adding ether, in colourless crystals which melt indefinitely at about  $120^\circ$ . The *phenylhydrazone*,  $C_{13}H_{12}N_2O_3$ , of 1:2:3:4-trihydroxybenzaldehyde (*Abstr.*, 1898, i, 581) forms yellow leaflets which melt at  $161^\circ$ .

2:4:5-*Trihydroxybenzaldehyde*, prepared from hydroxyquinol (Thiele, *Abstr.*, 1898, i, 469) crystallises from water in thick, pointed prisms, and melts at  $223^\circ$ ; with ferric chloride, it produces an intensely green coloration, which, in presence of caustic soda, becomes reddish brown, whilst with lead acetate and with baryta water it gives rise to yellow precipitates; the *phenylhydrazone*,  $C_{13}H_{12}N_2O_3$ , forms yellowish leaflets and melts at  $200^\circ$ .

W. A. D.

**Synthesis of Daphnetin and Æsculetin.** By LUDWIG GATTERMANN and M. KÖBNER (*Ber.*, 1899, 32, 287—288).—2 : 3 : 4-Trihydroxybenzaldehyde (Abstr., 1898, i, 581), when heated with sodium acetate and acetic anhydride during 5 hours at 170—180°, gives rise to diacetodaphnetin, which, on hydrolysis, yields daphnetin identical with the natural product : von Pechmann's views as to the structure of the latter (Abstr., 1884, 1173) are thus confirmed. By a similar reaction, 2:4:5-trihydroxybenzaldehyde (preceding abstract) is converted into the diacetyl derivative of æsculetin, which is thus shown to have the structure,  $C_6H_2(OH)_2 \begin{smallmatrix} & O & -CO \\ & | & | \\ CH & : & CH \end{smallmatrix} [(OH)_2 : O : CH = 1:2:4:5]$ , attributed to it by Will.

W. A. D.

**Electrolytic Decomposition of Orthonitrobenzoic Acid.** By CARL SCHALL (*Chem. Centr.*, 1898, ii, 1043; from *Arch. Sci. phys. nat. Genève* [iv], 6, 387—388).—When solutions of the salts of certain aromatic acids in the acids themselves are electrolysed, hydrocarbons are formed; such solutions are prepared by dissolving sodium carbonate in the dry molten acid. When a solution of 6·4 grams of sodium carbonate in 50 grams of orthonitrobenzoic acid at 160—180° is electrolysed by a current of 0·4—1 ampère, brown flakes, black carbonaceous substances, and small quantities of crystals which melt at 149—150° and have no acid properties are obtained. When water is present, nitrophenols are also formed.

E. W. W.

**New Derivatives of Gallic Acid.** By A. MAX HAMBURG (*Monatsh.*, 1898, 19, 593—608).—*Methylic bromotrimethylgallate*,  $C_6HBr(OMe)_3 \cdot COOMe$ , is prepared by adding bromine to methylic trimethylgallate dissolved in cooled, dry carbon tetrachloride; dry air is then driven through the liquid and the product distilled under diminished pressure. It is a colourless, highly dispersive, oily liquid, which boils at 202° under a pressure of 16 mm., and dissolves readily in the ordinary solvents, excepting water. When heated with potassium methoxide at 160° in sealed tubes, it is to a great extent decomposed, and a substance, probably *bromotrimethylgallic acid*,  $C_6HBr(OMe)_3 \cdot COOH$ , is formed in small quantity. This separates from alcohol, on the addition of water, as white, silky, shining needles, melts at 151°, and dissolves readily in alcohol and ether, less readily in benzene, and is insoluble in water.

*Methylic nitrotrimethylgallate*,  $NO_2 \cdot C_6H(OMe)_3 \cdot COOH$ , is prepared from methylic trimethylgallate, dissolved in acetic anhydride, by the action of nitric acid saturated with nitrous acid. It crystallises in yellowish tablets, melts at 67°, and dissolves readily in alcohol and ether, but is nearly insoluble in water, and in dilute potash.

When methylic nitrotrimethylgallate is heated with an alcoholic solution of stannous chloride, it is quickly reduced, and the *stannochloride* of the product separates in a crystalline form. The *hydrochloride* of methylic amidotrimethylgallate separates from methylic alcohol in pyramidal crystals belonging to the rhombic system [ $a:b:c=1:0\cdot6486:0\cdot9490$ ]; it is insoluble in ether, but dissolves

readily in water or alcohol, and the solution in the latter has a blue fluorescence; it melts at  $167^{\circ}$ . *Methylic amidotrimethylgallate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}(\text{OMe})_3 \cdot \text{COOMe}$ , crystallises from a mixture of benzene and light petroleum in well-formed, faintly-coloured crystals belonging to the monoclinic system [ $a : b : c = 0.3998 : 1 : 0.2917$ ,  $ac = 97^{\circ} 14'$ ]. It is readily soluble in alcohol, ether, and benzene, and dissolves in warm petroleum, but is only very sparingly soluble in water; it melts at  $41^{\circ}$ .

*Methylic hydroxytrimethylgallate*,  $\text{OH} \cdot \text{C}_6\text{H}(\text{OMe})_3 \cdot \text{COOMe}$ , obtained by warming the solution of the corresponding diazo-compound, separates from a mixture of methylic alcohol and light petroleum in colourless crystals melting at  $85^{\circ}$ . It is nearly insoluble in water, but dissolves readily in alcohol, ether, and benzene, and sparingly in methylic alcohol and light petroleum. *Hydroxytrimethylgallic acid*,  $\text{OH} \cdot \text{C}_6\text{H}(\text{OMe})_3 \cdot \text{COOH}$ , is purified by conversion into the corresponding calcium salt, from which it may be recovered by the addition of hydrochloric acid. It crystallises from boiling petroleum in slender, silky, white needles, which gradually become coloured on exposure to the air; it melts and decomposes at  $191^{\circ}$ , is sparingly soluble in water or light petroleum, but dissolves readily in warm alcohol, ether, benzene, or alkalis. Both the acid and its methylic salt yield gallic acid when heated with hydriodic acid at  $127$ — $135^{\circ}$ .

A. L.

**Preparation of Homophthalic Acid [Orthocarboxyphenylacetic Acid] and  $\beta$ -Hydrindone from the Indene of Coal Tar.** By FRIEDRICH HEUSLER and HEINRICH SCHIEFFER (*Ber.*, 1899, 32, 28—34).—Some of the fraction of coal-tar oil which is rich in indene is made into an emulsion with water by means of a mechanical stirrer, and a slight excess of 6 per cent. potassium permanganate is added gradually, no heat being employed. The product is filtered, and the filtrate shaken with benzene; the orthocarboxyphenylacetic (homophthalic) acid is then obtained by prolonged extraction with ether. The method is probably an advantageous one for the preparation of the acid. If cooling with ice is employed during the oxidation, a certain amount of hydrindeneglycol is formed; it can be separated by extraction with chloroform.

When chlorhydroxyhydrindene, obtained by chlorinating this fraction of coal-tar oil and then boiling it with water, is boiled with methyl alcoholic sodium methoxide, it forms the *hydrindeneglycol monomethylic ether*,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CH}(\text{OMe}) \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{CH} \cdot \text{OH}$ ; this boils at  $150$ — $151^{\circ}$  under a pressure of 13.5 mm., and has a sp. gr. = 1.12 at  $20^{\circ}$ ; when boiled for a short time with 25 per cent. sulphuric acid, it yields  $\beta$ -hydrindone,  $\text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CH} \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{CO}$ . If this is left in contact for 2 days with very dilute caustic soda, it forms *anhydrobis- $\beta$ -hydrindone*,  $\text{C}_9\text{H}_{14}\text{O}$ , melting at  $170^{\circ}$ , and when treated, in alcoholic solution, with amyl nitrite and a little hydrochloric acid, it yields *di-isonitroso- $\beta$ -hydrindone*, melting and decomposing at  $233^{\circ}$ . When the hydrindone is dissolved in fuming nitric acid and the solution poured into water, yellow 4-nitro-

$\beta$ -hydrindone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \left\langle \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \right\rangle \text{CO}$ , melting at  $141-141.5^\circ$  is formed; this dissolves in caustic soda, forming a deep purple-red solution; when left with dilute nitric acid for a day, 1:2:4-nitrophthalic acid is obtained, but if it is oxidised with chromic acid in acetic acid solution 1:2:4-nitro-orthocarboxyphenylacetic acid,  $\text{COOH} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3 \cdot \text{CH}_2 \cdot \text{COOH}$ , is formed as an intermediate product. C. F. B.

**Isomeric Forms of Ethylic Benzylidenebisacetoacetate.** By ROBERT SCHIFF (*Ber.*, 1899, 32, 332-337).—Besides the ordinary form of diethylic benzylidenebisacetoacetate,  $\text{CHPh}(\text{CHAc} \cdot \text{COOEt})_2$ , which melts at  $151^\circ$  (Hantzsch, *Abstr.*, 1886, 77), a second form has recently been prepared by Rabe (this vol., i, 289) from the sodium salt, an observation which is confirmed by the author in the present paper. He shows further that the three substances melting at  $150^\circ$ ,  $134^\circ$ , and  $120^\circ$ , which he obtained by the action of sodium ethoxide on the three modifications of ethylic benzylideneanilinoacetoacetate melting at  $104^\circ$ ,  $78^\circ$ , and  $95^\circ$  (*Abstr.*, 1898, i, 355), are different forms of ethylic benzylidenebisacetoacetate, and not of ethylic phenylcarbinolacetoacetate, as was previously supposed. In the preparation of ethylic benzylidenebisacetoacetate by the condensation of benzaldehyde with ethylic acetoacetate in presence of a trace of piperidine or of dipropylamine, the author states that the three modifications melting at  $150^\circ$ ,  $134^\circ$ , and  $120^\circ$  are all produced, together with an isomeric mixture melting at  $90-112^\circ$ . All the different modifications, on boiling with acetic anhydride, are converted into the form melting at  $151^\circ$ . The constitution of the different modifications has not been ascertained. T. M. L.

**Action of Ethylic Acetoacetate on Benzidine.** By KARL HEIDRICH (*Monatsh.*, 1898, 19, 690-706).—Ethylic acetoacetate unites with benzidine at  $100^\circ$ , forming the compound,  $2\text{C}_{12}\text{H}_8(\text{NH}_2)_2 \cdot \text{C}_6\text{H}_{10}\text{O}_3$ , which crystallises in small, yellow plates melting at  $128^\circ$ . At  $120^\circ$ , however, diacetoacetic benzidide,  $\text{C}_{12}\text{H}_8(\text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Ac})_2$ , is formed by elimination of water; this crystallises in thin, lustrous needles, melts and decomposes at  $233-235^\circ$ , and is sparingly soluble in the usual solvents. It gives a violet coloration with alcoholic ferric chloride, and reduces ammoniacal silver oxide. Bromine converts it into a dibromo-derivative,  $\text{C}_{20}\text{H}_{18}\text{Br}_2\text{N}_2\text{O}_4$ , which crystallises in small, lustrous needles, and decomposes at about  $250^\circ$ . It contains two atoms of replaceable hydrogen, and yields a sodium derivative, which crystallises in small needles, is decomposed by water, and with ethylic iodide yields the diethyl derivative, which melts and decomposes above  $300^\circ$ . The monophenylhydrazone,  $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_3$ , forms white, granular crystals, and decomposes at  $250^\circ$ . When treated with concentrated sulphuric acid in the cold, diacetoacetic benzidide is converted into dihydroxydilepidine,  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$ , which is an amorphous, white powder, melts above  $300^\circ$ , and gives no coloration with ferric chloride.

Monacetoacetic benzidide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Ac}$ , is always formed in small amount in the interaction of ethylic acetoacetate with benzidine; it is soluble in acids and can thus be separated from the insoluble diacetoacetic benzidide. It forms small, granular crystals,



decomposes at  $300^{\circ}$ , and gives a violet coloration with ferric chloride. The *hydrochloride*, *sulphate*, and *nitrate* are crystalline, and dissolve sparingly in water. When treated with sulphuric acid, it yields 3-*amido-phenyl-2'-hydroxylepidine*,  $C_{16}H_{14}N_2O$ , which forms white granules and gives a violet coloration with ferric chloride. A. H.

**Orthophenylbenzaldehyde.** By RICHARD FANTO (*Monatsh.*, 1898, 19, 584—592).—*Orthophenylbenzaldehyde*,  $C_{13}H_{10}O$ , is made by heating an intimate mixture of calcium orthophenylbenzoate with calcium formate, a considerable quantity of diphenyl being formed simultaneously. It is a pale, yellowish-green, odourless liquid, denser than water, and dissolves in all proportions in alcohol, ether, chloroform, and benzene, but only very sparingly in water; it boils at  $184^{\circ}$  under 21 mm. pressure. When oxidised with chromic acid, it yields orthophenylbenzoic acid. The *oxime*,  $C_{12}H_9 \cdot CH : NOH$ , has a faint, fruity odour, crystallises from ether in slender, white needles, and melts at  $115^{\circ}$ ; it dissolves readily in alcohol, ether, chloroform, and benzene, but is insoluble in water. The *phenylhydrazone*,  $C_{12}H_9 \cdot CH : N \cdot NHPh$ , which is very unstable, crystallises from cooled ether in shining leaflets and melts at  $118$ — $124^{\circ}$ .

When an alcoholic solution of orthophenylbenzaldehyde is treated with sodium amalgam, care being taken that the liquid remains neutral, and this is subsequently extracted with ether, a crystalline substance,  $C_{26}H_{18}O$ , and an oil are obtained; the crystalline substance separates from alcohol in small, glistening crystals, has a pleasant, rose-like odour, and melts at  $111^{\circ}$ , decomposing at higher temperatures; it dissolves very readily in ether and light petroleum, but only sparingly in alcohol. The oil, when treated with acetic anhydride and submitted to distillation, yields *orthophenylbenzylic acetate*,  $C_{12}H_9 \cdot CH_2 \cdot OAc$ , a thick, odourless, pale yellow oil which boils at  $182^{\circ}$  under 20 mm. pressure; it is miscible with ether, alcohol, and petroleum, but insoluble in water. *Orthophenylbenzylic alcohol*,  $C_{12}H_9 \cdot CH_2 \cdot OH$ , prepared by hydrolysing the acetate with water at  $130^{\circ}$ , is a colourless, oily liquid, having an aromatic odour, and boils at  $181^{\circ}$  under 8 mm. pressure; it dissolves in all proportions in alcohol, ether, and benzene, but is insoluble in water. A. L.

**Two Isomeric Chlorodiphenacyls.** By CARL PAAL and HERMANN STERN (*Ber.*, 1899, 32, 530—531. Compare Paal and Demeler, *Abstr.*, 1896, 1, 687).—Chlorodiphenacyl,  $C_{16}H_{13}ClO_2$ , melting at  $117^{\circ}$ , is prepared, according to Staedel and Rügheimer's directions, by the action of ammonia on an ethereal solution of chloracetophenone; it can also be obtained by the action of alcoholic sodium ethoxide on chloracetophenone. The isomeride melts at  $154$ — $155^{\circ}$ , and both compounds yield diphenacyl on reducing the alcoholic solutions with zinc dust. M. O. F.

**Iododiphenacyl.** By CARL PAAL and HERMANN STERN (*Ber.*, 1899, 32, 532—533).—*Phenacylic iodide* (*o*-iodacetophenone),  $COPh \cdot CH_2I$ , is prepared by the action of aqueous potassium iodide on an alcoholic solution of chloracetophenone or bromacetophenone; it dissolves very readily in organic solvents, and has not been obtained pure.

*Iododiphenacyl*,  $C_{16}H_{13}IO_2$ , obtained by treating the foregoing substance with alcoholic sodium ethoxide, crystallises from alcohol in slender needles and melts at  $215^\circ$ . M. O. F.

**Derivatives of Benzophenone.** By PIETRO BARTOLOTTI (*Gazzetta*, 1898, 28, ii, 283—290).—*Benzoylcreosol benzoate*,  $C_6H_2BzMe(OMe) \cdot OBz$  [Me : OMe : OBz = 1 : 3 : 4], prepared by the action of creosol benzoate on benzoic chloride in presence of zinc chloride, forms white crystals melting at  $95$ — $96^\circ$ .

*Benzoylcreosol*,  $C_6H_2BzMe(OMe) \cdot OH$ , obtained by hydrolysing a hot alcoholic solution of benzoylcreosol benzoate with hot dilute alcoholic caustic soda, forms white crystals melting at  $150^\circ$ ; it is soluble in the ordinary solvents but insoluble in water. It dissolves in sodium hydroxide solution, giving an intensely yellow liquid from which it is thrown down in the crystalline state by carbonic anhydride. Ferric chloride added to its dilute alcoholic solution produces a greenish coloration.

*Benzoylcreosol acetate*,  $C_6H_2BzMe(OMe) \cdot OAc$ , produced by the action of acetic anhydride on benzoylcreosol in presence of fused sodium acetate, separates from alcohol in white crystals melting at  $77$ — $5^\circ$ .

*Benzoylmethylcreosol*,  $C_6H_2BzMe(OMe)_2$ , obtained by the action of methyl alcoholic potash and methylic iodide on benzoylcreosol, was not obtained crystalline. T. H. P.

**New Syntheses in the Flavone Group.** By STANISLAUS VON KOSTANECKI (*Chem. Centr.*, 1898, ii, 1060; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 403—404).—Orthohydroxybenzylideneacetophenone dibromide, when treated with alcoholic potash, yields flavone, and, similarly, 2-bromoflavone is obtained from 5-bromo-2-hydroxybenzylideneacetophenone dibromide. Attempts to prepare 3:4-dihydroxyflavone from piperonal-2-hydroxyacetophenone dibromide resulted in the formation of piperonalcoumaranone, and 2-hydroxyanisalacetophenone dibromide and piperonalresacetophenone methylic ether yielded similar compounds and not flavone derivatives (compare the following abstracts). E. W. W.

**Ethoxy- and Methoxy-piperonalcoumaranone.** By T. EMILEWICZ and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 309—314. Compare Abstr., 1898, i, 369).—The compound,  $C_{18}H_{14}O_5$ , described by the authors as a product of the action of alcoholic potash on the acetyl derivative of piperonalresacetophenone ethylic ether, is shown to be 3-ethoxypiperonalcoumaranone,  $OEt \cdot C_6H_3 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown CO \diagup \end{smallmatrix} C : CH \cdot C_6H_3 \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} CH_2$ ; thus the piperonal compound differs from the corresponding benzylidene compound by condensing to a 5-, and not to a 6-membered, ring. The substance crystallises from alcohol in long, straw-coloured needles, melts at  $150^\circ$ , and dissolves in concentrated sulphuric acid with an eosin-red colour.

*Benzylidenepaeonol* [4-methoxy-2-hydroxyphenyl styryl ketone],  $OMe \cdot C_6H_3(OH) \cdot CO \cdot CH : CHPh$ , separates from alcohol in long, deep-yellow needles which melt at  $105^\circ$ , and are coloured red by concentrated sulphuric acid. The *acetyl*

derivative crystallises from alcohol in pale yellow needles melting at 83—84°, and yields a colourless *dibromide* melting at 130·5—131·5°. The *dibromide* is converted, by the action of alcoholic potash, into 3-methoxy-flavone,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{CPh} \\ | \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ ; this crystallises from alcohol in colourless needles melting at 110—111°, and like 3-ethoxyflavone, shows a very characteristic blue fluorescence when dissolved in concentrated sulphuric acid.

*Piperonalpaeonol* [4-methoxy-2-hydroxyphenyl piperonalmethyl ketone],  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{CH}_2$ , crystallises from alcohol in long, yellow needles which melt at 148·5°, and are coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises from alcohol in yellow needles melting at 158—159°, and yields a *dibromide* which crystallises from a mixture of chloroform and ether in colourless needles melting at 137—138°. By the action of alcoholic potash, the *dibromide* is converted into 3-methoxypiperonalcoumaranone; this has already been prepared by Friedländer and Brüll (Abstr., 1897, i, 221), but was described by them as a flavone derivative; it crystallises from alcohol in yellow needles, melts at 176°, and dissolves in concentrated sulphuric acid with an eosin-red colour.

The flavones are readily decomposed by sodium ethoxide in alcoholic solution, yielding a hydroxy-ketone and an aromatic acid; the isomeric coumaranone derivatives are converted into insoluble resins.

T. M. L.

*Piperonalcoumaranone*. By W. FEUERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 315—317. Compare preceding abstract).—*Piperonal-2'-hydroxyacetophenone* [*orthohydroxyphenyl piperonalmethyl ketone*],  $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{CH}_2$ , crystallises from alcohol in deep-yellow needles which melt at 137—138°, and are coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises from dilute alcohol in pale yellow needles melting at 95—96·5°, and yields a *dibromide* which crystallises from ether in colourless prisms melting at 113—114°. By the action of alcoholic potash, the *dibromide* is converted into *piperonalcoumaranone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C} : \text{CH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{CH}_2$ ; this crystallises from glacial acetic acid in deep-yellow needles melting at 192°; the crystals are coloured deep-red by concentrated sulphuric acid and yield an eosin-red solution; the substance is identical with that previously described by Friedländer and Neudörfer (Abstr., 1897, i, 425) as methylenedihydroxyflavone.

T. M. L.

4-Methoxybenzylidenecoumaranone. By F. HERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 318—321. Compare preceding abstracts).—*Anisylidene-2-hydroxyacetophenone* [*orthohydroxyphenyl paramethoxystyryl ketone*],  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , crystallises from alcohol in bright, orange-coloured plates, melts at 93—94°, and is coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises in colourless prisms melting at 84°, and

yields a *dibromide* which crystallises from a mixture of chloroform and ether in white, silky needles melting at 104—105°. By the action of alcoholic potash, the dibromide is converted into *para-anisylidenecoumaranone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , which crystallises from alcohol in long, yellow needles melting at 133·5—134·5°; the crystals are coloured red by concentrated sulphuric acid, and yield an orange-coloured solution.

*4-Ethoxybenzylidene-2-hydroxyacetophenone* [*orthohydroxyphenyl par-ethoxystyryl ketone*] crystallises from alcohol in yellow needles, melts at 61°, and is coloured red by concentrated sulphuric acid. The *acetyl* derivative crystallises from dilute alcohol in pale yellow flakes, and melts at 68°, but the dibromide has not yet been obtained in a crystalline form.

T. M. L.

**3:4'-Dihydroxyflavone.** By STANISLAUS VON KOSTANECKI and F. W. OSIUS (*Ber.*, 1899, **32**, 321—325. Compare Abstr., 1898, i, 369 and 583).—*Anisylidenepaeonol* [*4-methoxy-2-hydroxyphenyl paramethoxystyryl ketone*],  $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , crystallises in yellow needles, and melts at 113—114°; the crystals are coloured red by concentrated sulphuric acid, and give an orange-coloured solution. The *acetyl* derivative crystallises from alcohol in pale-yellow needles, and melts at 103—104°. The corresponding *4-ethoxy*-compound crystallises from alcohol in yellow needles and melts at 110—111°; the crystals are coloured red by concentrated sulphuric acid, and dissolve in it, yielding an orange-coloured solution. The *acetyl* derivative crystallises from alcohol in short, thick needles melting at 75°, and yields a *dibromide* which crystallises from a mixture of chloroform and ether in colourless needles melting at 130—131°. By the action of alcoholic potash, the dibromide is converted into *3-ethoxy-4'-methoxyflavone*,  $\text{OEt}\cdot\text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{C}_6\text{H}_4\cdot\text{OMe}$ ; when purified

by repeated crystallisation, this is obtained in colourless crystals melting at 144—145°, and gives an intense blue fluorescence with concentrated sulphuric acid; it is, however, somewhat difficult to free it from the isomeric coumaranone derivative which is produced in small quantities during the action. When boiled with an alcoholic solution of sodium ethoxide, it is decomposed in the normal way into *4-ethoxy-2-hydroxyacetophenone*. If heated with concentrated hydriodic acid, it yields *3:4'-dihydroxyflavone*,  $\text{HO}\cdot\text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} \text{C}:\text{C}_6\text{H}_4\cdot\text{OH}$ ;

this melts at 315°, and dissolves in caustic soda, forming a yellow solution with a pale-green fluorescence; its solution in sulphuric acid is colourless, but shows an intense blue fluorescence; the *diacetyl* derivative crystallises from alcohol in white, silky needles and melts at 182—183°.

T. M. L.

**Synthesis of 2-Hydroxyflavone.** By STANISLAUS VON KOSTANECKI, R. LEVI, and J. TAMBOR (*Ber.*, 1899, **32**, 326—332).—*Quinacetophenone monethylic ether* [*5-ethoxy-2-hydroxyacetophenone*],  $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Ac}\cdot\text{OH}$ , crystallises from alcohol in yellow prisms and melts at 57°, whilst

2:5-diethoxyacetophenone crystallises in the triclinic system [ $a:b:c = 0.8630:1:0.829$ ;  $\alpha = 87^\circ 45'$ ,  $\beta = 119^\circ 15'$ ,  $\gamma = 82^\circ 45'$ ] and melts at  $42^\circ$ . By condensation with benzaldehyde, the latter substance gives 2:5-diethoxyphenyl styryl ketone,  $\text{C}_6\text{H}_3(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$ , which crystallises from alcohol in yellow prisms, and melts at  $50\text{--}51^\circ$ . The monethylic ether, however, gives 2-ethoxyflavanone,

$\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{O} \text{---} \text{CHPh} \\ \diagdown \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$ , which crystallises from alcohol in long, glistening needles, melts at  $103^\circ$ , and shows a blue fluorescence in dilute alcoholic solution. By the action of bromine, it gives bromo-

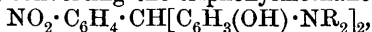
2-ethoxyflavanone,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{CO} \end{smallmatrix} > \text{C}_2\text{H}_2\text{BrPh}$ , which crystallises from alcohol in colourless flakes and melts at  $98\text{--}99^\circ$ . When treated with alcoholic potash, the bromo-compound loses a molecule of hydrogen

bromide and gives 2-ethoxyflavone,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{O} \text{---} \text{CPh} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix}$ ; this crystallises from alcohol and from light petroleum in needles, and from benzene in prisms, melts at  $146\text{--}147^\circ$ , and its solution in sulphuric acid shows a green fluorescence. It is decomposed in the normal way by sodium ethoxide, giving benzoic acid and 5-ethoxy-2-hydroxyacetophenone, whilst with hydriodic acid it gives 2-hydroxyflavone,

$\text{OH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \diagup \text{O} \text{---} \text{CPh} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix}$ ; this crystallises from alcohol in colourless needles, melts at  $231\text{--}232^\circ$ , shows a green fluorescence in sulphuric acid solution, and gives an acetyl derivative which crystallises in white, silky needles, and melts at  $157\text{--}158^\circ$ . T. M. L.

**Condensation of Nitrobenzaldehyde with Gallacetophenone.** By HANS RUPE and J. LEONTÉEFF (*Chem. Centr.*, 1898, ii, 1043; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 390—391).—When a mixture of gallacetophenone (1 mol.) with meta- or para-nitrobenzaldehyde (1—2 mols.) and zinc chloride is heated at  $90\text{--}100^\circ$ , a compound,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}[\text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})_3]_2$ , is obtained, which is not a derivative of triphenylmethane, as it is not oxidised by lead peroxide, and its colour reactions resemble those of gallacetophenone. The bases obtained by reducing this compound with stannous chloride yield azo-colours when diazotised and then condensed with phenols. E. W. W.

**Isomerides of the Rhodamines and the Pararhodamines.** By EMILIO NOELTING and PAIRA (*Chem. Centr.*, 1898, ii, 1049; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 397—399).—The rhodamines obtained by the action of phthalic anhydride on dialkyl derivatives of orthamidophenols, must be regarded as orthocarboxyl derivatives of diamidophenylpyrone, in which the hydrogen atoms of the amido-groups are replaced by alkyl groups. The meta- and para-isomerides have been prepared by condensing nitrobenzaldehyde with dialkylmetamidophenols, converting the triphenylmethane derivative,



so obtained into a pyrone derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{smallmatrix} \diagup \text{C}_6\text{H}_3(\text{NR}_2) \\ \diagdown \text{C}_6\text{H}_3(\text{NR}_2) \end{smallmatrix} > \text{O}$ , by eliminating water, then substituting carboxyl for the nitro-group,

and finally oxidising the leuco-base thus formed. These isomeric rhodamines have properties similar to those of ordinary rhodamines, and yield ethers corresponding with the anisolines. E. W. W.

**Meldola and Hughes' Perinaphthaquinone and Monobromindone.** By CARL LIEBERMANN and S. SCHLOSSBERG (*Ber.*, 1899, 32, 546—550).—The perinaphthaquinone described by Meldola and Hughes (*Trans.*, 1890, 393, 631, 808) as being formed by the action of nitric acid on dibromonaphthol is obtained in slightly better yield by using somewhat less nitric acid. It is found to be identical with the dinaphthaquinone,  $C_{20}H_{10}O_4$ , prepared by Witt and Dedichen (*Abstr.*, 1898, i, 144), since not only do the quinols and the acetyl derivatives of the quinols of both compounds agree in all their properties, but also on distilling the perinaphthaquinone with zinc dust, Watson Smith's iso- ( $\beta$ - $\beta$ ?)-dinaphthyl is produced. Probably also the dinaphthaquinone prepared by Staub and Watson Smith by oxidising isodinaphthyl is identical with this substance.

The chief product of the above reaction which Meldola and Hughes regarded as monobromindone, is in reality monobrom- $\alpha$ -naphthaquinone, since, on bromination, it gives dibrom- $\alpha$ -naphthaquinone melting at  $218^\circ$ , and not dibromindone, also, on treatment with ethylic sodiomalonate, it gives the blue coloration of halogenated  $\alpha$ -naphthaquinones and not the red colour which is characteristic of the chlorine and bromine derivatives of indone. J. F. T.

**The Naphthaquinone from Dibrom- $\alpha$ -Naphthol.** By RAPHAEL MELDOLA (*Ber.*, 1899, 32, 868—870. Compare Meldola, *Trans.*, 1890, 57, 631).—The author's investigation of the perinaphthaquinone obtained from dibrom- $\alpha$ -naphthol by the action of fuming nitric acid has led to the result indicated by Liebermann and Schlossberg (foregoing abstract). The fact that this compound is a derivative of dinaphthyl is established by the action of hydroxylamine hydrochloride, which gives rise to the monoxime of a dinaphthylquinone.

The *oxime*,  $C_{20}H_{10}O_3 \cdot NOH$ , forms reddish-brown leaflets, and cannot be recrystallised from common solvents; it changes colour at  $182$ — $184^\circ$ , but does not melt below  $306^\circ$ . It dissolves in dilute aqueous alkalis and alkali carbonates, yielding highly characteristic, blue solutions, from which acids precipitate the unaltered oxime; the blue colour of the alkaline solution changes to orange when zinc dust is added, being restored, however, on exposure to air. Concentrated sulphuric acid develops a green coloration which becomes violet on dilution.

The phenylhydrazone and anilide of the quinone have been prepared; the *compound* with orthophenylenediamine crystallises from nitrobenzene in yellowish needles, and does not melt below  $300^\circ$ .

As regards the production of bromindone from dibrom- $\alpha$ -naphthol (*Trans.*, 1890, 57, 393), the author states that the conditions peculiar to the original preparation of this compound have not been hitherto reproduced successfully. M. O. F.

**Synthesis of Hydroxyaldehydes of the Naphthalene Series.** By LUDWIG GATTERMANN and TH. VON HORLACHER (*Ber.*, 1899, 32, 284—286).—The hydroxy-derivatives of naphthalene yield aldehydes by

the method previously described (this vol., i, 363), with even greater ease than the monhydric phenols. 1:4-Hydroxynaphthaldehyde has already been described (Gattermann and Berchemann, Abstr., 1898, i, 581); the *imide-hydrochloride*,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH} : \text{NH} \cdot \text{HCl}$ , formed as an intermediate product in its preparation, is easily soluble in water and separates in colourless plates on adding ether to its solution in absolute alcohol. The *aniline* derivative,  $\text{C}_{17}\text{H}_{13}\text{NO}$ , of 1:4-hydroxynaphthaldehyde, crystallises from dilute alcohol in lustrous, golden-yellow needles, and melts at  $133^\circ$ ; the *phenylhydrazone*,  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$ , separates from glacial acetic acid in yellow needles and melts at  $119.5^\circ$ .

The *imide-hydrochloride*,  $\text{C}_{11}\text{H}_{10}\text{NOCl}$ , derived from  $\beta$ -naphthol, forms colourless needles, and is easily converted by warm water into 2-hydroxy-1-naphthaldehyde, which melts at  $81^\circ$ , not at  $76^\circ$  as stated by Kaufmann (Abstr., 1882, 1068). The *azine*,  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ , prepared from the latter, is very sparingly soluble in the usual solvents, and crystallises from nitrobenzene in golden-yellow needles which do not melt below  $290^\circ$ ; the condensation product,  $\text{C}_{17}\text{H}_{13}\text{NO}$ , which the aldehyde forms with aniline, crystallises from alcohol in yellow needles and melts at  $93^\circ$ , whilst the *phenylhydrazone*,  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$ , crystallises from acetic acid in golden plates, which darken and melt at  $205^\circ$ .

W. A. D.

**Colour Reactions of Indones and Quinones with Derivatives of Malonic Acid.** By CARL LIEBERMANN (*Ber.*, 1899, 32, 260—267. Compare this vol., i, 219).—*Bromindonemalononitrile*,  $\text{C}_{12}\text{H}_5\text{BrN}_2\text{O}$ , formed by the action of dibromindone on malononitrile in the presence of sodium ethoxide, crystallises in yellowish prisms melting at  $139^\circ$ ; it dyes wool reddish-brown. *Ethylic chlorindonemalonate*,  $\text{C}_{16}\text{H}_{15}\text{O}_5\text{Cl}$ , closely resembles the foregoing compound. *Ethylic brom- $\alpha$ -naphthaquinonemalonate*,  $\text{C}_6\text{H}_4 \cdot \text{CO} \begin{array}{c} \text{CO} - \text{CBr} \\ \diagup \quad \diagdown \end{array} \text{C} \cdot \text{CH}(\text{COOEt})_2$ , forms yellow crystals melting at  $102^\circ$ , and yields soluble blue alkali salts.

Ethylic brom- $\alpha$ -naphthaquinoneacetoacetate also forms yellow crystals and melts at  $98^\circ$ . When dibrom- $\alpha$ -naphthaquinone is treated in benzene solution with sodium ethoxide, *ethoxybrom- $\alpha$ -naphthaquinone*, melting at  $118^\circ$ , is formed together with the corresponding hydroxy-compound; the ethoxy-derivative is also formed by the action of ethylic ethylmalonate on dibromonaphthaquinone, and, moreover, reacts with ethylic malonate in the same way as dibromonaphthaquinone. *Ethylic bromo- $\beta$ -naphthaquinonemalonate* crystallises in reddish-brown needles, melts at  $96$ — $97^\circ$ , and forms a greenish-blue solution in alcoholic potash. *Ethylic 2-chlor- $\alpha$ -naphthaquinonemalonate* forms yellow crystals melting at  $82$ — $83^\circ$ . *Ethylic  $\beta$ -naphthaquinonemalonate* crystallises in golden-brown needles melting at  $107$ — $108^\circ$ .

The *anhydride* of *ethylic 3-acetamido- $\beta$ -naphthaquinonemalonate*,  $\text{CO} \begin{array}{c} \text{CO} - \text{C} \cdot \text{Nac} \\ \diagup \quad \diagdown \end{array} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH}(\text{COOEt})_2 \text{CO}$ , formed by the action of ethylic sodiomalonate on chloracetamido- $\beta$ -naphthaquinone, crystallises in reddish-brown needles which melt and decompose at  $234^\circ$ .

*Bischlorindonephloroglucinol*,  $C_6H(OH)_3(C \begin{smallmatrix} \text{CCl} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CO})_2$ , is a red substance which decomposes and melts at  $241^\circ$ , and yields a blue solution in alcoholic sodium ethoxide.

In the preparation of these compounds, it is necessary to avoid an excess of alkali. The reaction only succeeds with quinones which possess a replaceable hydrogen or halogen atom. Benzylic cyanide and ethylic cyanacetate, and, occasionally, deoxybenzoin and acetyl-acetone react in a manner similar to that of ethylic malonate.

A. H.

**Azo-dyes derived from 2':1-Naphthylaminesulphonic Acid.** By EMILIO NOELTING and BIANCHI (*Chem. Centr.*, 1898, ii, 1049—1050; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 399—400).—By the action of paranitrodiazobenzene in alkaline solution on 2':1-naphthylamine-sulphonic acid, a compound,  $SO_3H \cdot C_{10}H_6 \cdot NH \cdot N : N_2 \cdot C_6H_4 \cdot NO_2$  [ $SO_3H : NH = 1 : 2$ ], is obtained, which has all the properties of a diazoamido-compound, and dyes silk and wool yellow. When the action takes place in an acid solution, however, an azo-compound,  $SO_3H \cdot C_{10}H_5(NH_2) \cdot N_2 \cdot C_6H_4 \cdot NO_2$  [ $SO_3H : NH_2 : N_2 = 1 : 2' : 1$ ], is formed, which dyes wool purplish-red, and when reduced yields a naphthyl-enediaminesulphonic acid.

E. W. W.

**Preparation of a Hydroxynaphthaquinonesulphonic Acid from Naphthol-yellow-S.** By FRANZ GAESS (*Ber.*, 1899, 32, 231—241).—Lauterbach has stated (*Abstr.*, 1882, 63) that, on reduction with tin and hydrochloric acid, naphthol-yellow-S (2:4-dinitro-1:2'-naphtholsulphonic acid) gives rise to the double salt [ $OH \cdot C_{10}H_4(NH_2)_2 \cdot SO_3$ ] $_2$ Sn, 2HCl, 4SnCl $_2$ ; the diamido-acid is, however, obtained free from tin when the reduction is carried out rapidly with little more than the theoretical amount of the metal, and a considerable excess of hydrochloric acid. 2:4-Diamido-1:2'-naphtholsulphonic acid is, however, most conveniently prepared by shaking the dinitro-compound, in successive small quantities, with an aqueous solution of sodium hydrogen sulphite containing the zinc-dust theoretically necessary to convert the latter into hyposulphite; on filtering the solution thus obtained into hydrochloric acid, the *hydrochloride*,  $C_{10}H_{10}N_2SO_4 \cdot HCl$ , separates in nearly colourless, rhombic plates. This is somewhat easily soluble in water, but is precipitated on adding hydrochloric acid; it dissolves in caustic soda, aqueous ammonia, and baryta-water, giving solutions which rapidly become red. When warmed with acetic anhydride and sodium acetate, it gives rise to *sodium triacetyldiamidonaphtholsulphonate*, which is insoluble in alcohol, but soluble in water; on adding barium chloride to the aqueous solution, the *salt*,  $(C_{16}H_{15}N_2O_7S)_2Ba + 3\frac{1}{2}H_2O$ , separates in white, stellar aggregates of needles, which are only sparingly soluble in cold water, but more readily in hot.

Amidonaphthaquinoneimidesulphonic acid (Lauterbach, *loc. cit.*) separates as a red, crystalline powder on blowing air through a cold ammoniacal solution of 2:4-diamido-1:2'-naphtholsulphonic acid, and in the form of lustrous scales on adding sodium nitrite to a solution



of the same substance in hydrochloric acid. It dissolves in concentrated sulphuric acid, but is precipitated unchanged on adding water; it does not form a compound with hydrogen chloride, but yields an *ammonium* salt in red crystals easily soluble in water, and a *barium* salt,  $(C_{10}H_7N_2SO_4)_2Ba$ , which is sparingly soluble in water, and forms microscopic, red leaflets. When amidonaphthaquinoneimidesulphonic acid is dissolved in 30 per cent. aqueous caustic soda, it gives rise initially to a separation of lustrous, golden needles, but after a time is decomposed with evolution of ammonia; when boiled during 7 hours with water, it is completely dissolved, and, on adding barium chloride, a crystalline precipitate of *barium hydroxynaphthaquinoneimidesulphonate* or *amidonaphthaquinonesulphonate*,  $(C_{10}H_6NSO_5)_2Ba$ , separates. On boiling amidonaphthaquinoneimidesulphonic acid with aqueous ammonia during 3 hours, and subsequently adding hydrochloric acid, a dark-coloured, crystalline powder having a slight metallic lustre is precipitated; this easily dissolves in water, and is oxidised by ferric chloride to a violet coloured acid-dye.

When ferric chloride is added to an aqueous solution of barium triacetyldiamidonaphtholsulphonate, acidified with acetic acid, *barium 2-acetamido-1:4:2'-naphthaquinonesulphonate*,  $(C_{12}H_8NSO_6)_2Ba + \frac{1}{2}H_2O$ , separates in golden needles; this is very sparingly soluble in water, but the corresponding *sodium* salt,  $C_{12}H_8NSO_6Na + 3H_2O$ , prepared similarly, readily dissolves in warm water, and crystallises in long, yellowish-red needles; in preparing these salts, isomerides do not appear to be formed. When the sodium salt is heated with aqueous caustic soda or with dilute hydrochloric acid, the acetamido-group is displaced by hydroxyl, 2-hydroxy-1:4:2'-naphthaquinonesulphonic acid (*infra*) being formed; when warmed with an aqueous solution of aniline acetate or hydrochloride, the *aniline* salt,  $C_{18}H_{16}N_2SO_6 + 3H_2O$ , separates in golden crystals, whilst orthophenylenediamine gives rise, under similar conditions, to the salt,  $C_{16}H_{15}N_3SO_5 + H_2O$ , derived from amidonaphthaquinonesulphonic acid; as eurhodine is not formed in the latter case, the acetamido-group in the original sodium salt must occupy position 2.

2-Hydroxy-1:4:2'-naphthaquinonesulphonic acid is formed when amidonaphthaquinoneimidesulphonic acid is boiled for 3 hours with dilute hydrochloric acid; the *normal barium* salt,  $C_{10}H_4SO_6Ba + 3\frac{1}{2}H_2O$ , separates in the form of long, yellowish-red needles when a similar decomposition is effected by boiling with baryta-water. The *barium hydrogen* salt,  $(C_{10}H_5SO_6)_2Ba + 2H_2O$ , separates from water in yellow needles, the *sodium hydrogen* salt,  $C_{10}H_5SO_6Na + 3H_2O$ , in bright-yellow six-sided plates, and the *normal sodium* salt,  $C_{10}H_4SO_6Na_2$ , in brownish-red crystals. When the sodium hydrogen salt is boiled with aniline in aqueous or alcoholic solution, it gives rise to the *aniline* salt,  $C_{22}H_{18}N_2SO_5$ , of an *anilidonaphthaquinonesulphonic acid*; this crystallises from water or dilute ammonia in beautiful, lustrous, crimson leaflets, and, when acted on by aqueous barium chloride, forms the red *barium* salt,  $(C_{16}H_{10}NSO_5)_2Ba$ , by the removal of aniline. When aqueous solutions of sodium hydroxynaphthaquinonesulphonate and orthophenylenediamine are mixed, and acetic acid subsequently added, orange-yellow crystals separate, which apparently consist

of the eurhodolesulphonic acid,  $C_6H_4 \begin{matrix} \text{N}=\text{C} \\ \text{NH}\cdot\text{C} \end{matrix} \begin{matrix} \text{---} \\ \text{CH}\cdot\text{CO} \end{matrix} \begin{matrix} \text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{SO}_3\text{H} \\ \text{C}\cdot\text{CH}\cdot\text{CH} \end{matrix}$ ; this is almost insoluble in boiling water, but dissolves unchanged in concentrated sulphuric acid, giving a crimson solution, and is not decomposed when heated with concentrated hydrochloric acid during several hours at  $200^\circ$ ; it dissolves in aqueous caustic soda, yielding the *sodium* salt, which forms red crystals, and is easily soluble in water. When aqueous solutions of phenylorthophenylenediamine and sodium hydroxynaphthaquinonesulphonate are mixed in molecular proportion, a brownish, crystalline precipitate is formed, which apparently consists of 1 : 4 : 2 : 7-rosindonesulphonic acid. W. A. D.

**Oleum Cadi.** By JULIUS TROEGER and P. FELDMANN (*Arch. Pharm.*, 1898, 236, 692—696).—The authors have attempted to prepare cadinene from *Oleum cadi* according to Wallach's method, in order to compare it with the oil obtained from the essential oil of angostura bark (Beckurts and Troeger, this vol., i, 64); they find, however, that the *Oleum cadi* examined by them contained very little cadinene. The fraction boiling at  $260$ — $280^\circ$  consisted of a mixture of substances which could not be isolated in a pure form. An optically inactive sesquiterpene,  $C_{15}H_{24}$ , boiling at  $250$ — $260^\circ$  was obtained, but it gave no solid derivatives with hydrogen chloride or hydrogen bromide. J. J. S.

**Extraction and Synthesis of the Odoriferous Principle or Jasmine.** By ALBERT VERLEY (*Compt. rend.*, 1899, 128, 314—317).—By allowing repeatedly renewed jasmine blossoms to exhale their perfume between sheets of glass coated with grease (*enfleurage à froid*) and finally extracting the latter with vaseline oil, the fat remains undissolved whilst the odoriferous principle is removed; this is then isolated by shaking with acetone, evaporating the solution so obtained, and fractionally distilling the product. In this way, a light-yellow oil is obtained which boils at  $100$ — $101^\circ$  under 12 mm. pressure, possesses an intense odour of jasmine, has a sp. gr. =  $1\cdot1292$  at  $0^\circ$ , and, although containing a small quantity of linalool, has a composition approximately corresponding with that required for the formula  $C_9H_{10}O_2$ . The oil, to which the name *jasmal* is given, yields benzoic acid when oxidised with chromic acid, the odour of formaldehyde becoming perceptible during the process; when boiled with water (100 c.c.) containing oxalic acid (1 gram) during several hours, it forms phenylglycol. From these facts, it appears to consist of the *methylenic acetal*,  $\begin{matrix} \text{CH}_2-\text{O} \\ \text{CHPh}\cdot\text{O} \end{matrix} > \text{CH}_2$ , of phenylglycol, and can be prepared synthetically by warming the latter (50 grams) on the water-bath with water (300 c.c.), sulphuric acid (125 grams), and formaldehyde (100 c.c.); thus prepared, it boils at  $101^\circ$  under 12 mm. pressure, at  $218^\circ$  under atmospheric pressure, has a sp. gr. =  $1\cdot1334$  at  $0^\circ$ , and a refractive index  $\mu_D = 1\cdot519$ .

The corresponding *ethylidene* and *amylidene* acetals of phenylglycol are prepared in the same manner and have similar properties; the

*acetal*,  $\begin{matrix} \text{CH}_2\cdot\text{O} \\ \text{CH}_2\cdot\text{O} \end{matrix} > \text{CHPh}$ , prepared by Fischer and Giebe's method (Abstr., 1898, i, 167), boils at  $140^\circ$ . W. A. D.

**Ethereal Oil of Jasmine Flower.** By ALBERT HESSE and FRIEDRICH MÜLLER (*Ber.*, 1899, 32, 565—574).—As the result of a large number of experiments on the essential oil of the Jasmine flower, which Verley claims to have prepared synthetically by the condensation of phenylglycol and formaldehyde (preceding abstract), the authors are unable to understand how this investigator arrived at his conclusions. No trace of phenylglycol could be detected after heating the ethereal oil with oxalic acid, although this glycol is especially easy to isolate from its methyleneacetal. The essential oil contains no trace of phenylglycolmethyleneacetal, but consists of a mixture of ethylic benzylacetate and a salt of terpene alcohol, together with two other substances of unknown constitution to which this flower owes its characteristic smell. The formation of benzaldehyde, formaldehyde, and benzoic acid in Verley experiments was due to the ethylic benzylacetate. J. F. T.

**The Molecular Weight of Digitogenin and its Decomposition Products.** By ALBERT EDINGER (*Ber.*, 1899, 32, 339—341).—The author has determined the molecular weights of digitonin, digitogenin and their oxidation products, digitogenic acid, hydrodigitonic acid, and digitic acid by the boiling point method, and finds them to be twice that indicated by the formulæ usually accepted; these must, therefore, be doubled, and the acids in question must be considered dibasic instead of monobasic. J. F. T.

**Anabsinthin.** By ADRIAN and AUGUSTE TRILLAT (*Compt. rend.*, 1899, 128, 115—117).—*Artemisia absinthium* contains a compound *anabsinthin*,  $\text{C}_{18}\text{H}_{24}\text{O}_4$ , soluble in alcohol, benzene, and chloroform, but only slightly soluble in water; this forms long, white, prismatic needles, which, when dried at  $120^\circ$ , melt at  $258$ — $259^\circ$ ; from acetone, it separates in large and peculiar crystals. With sulphuric acid, it gives a violet-red coloration that changes to blue, and with dilute hydrochloric acid (1:5), it gives a brown coloration and shows a slight green fluorescence when water is added. Acetic anhydride converts anabsinthin into a resin, but oxidising and reducing agents, and dilute acids and alkalis, have but little action on it. It does not reduce Fehling's solution, and yields no compound with phenylhydrazine. When distilled, it yields acetic and formic acids and an oil which becomes green and blue when exposed to air. Anabsinthin is quite distinct from the absinthin of Senger and of Bourcet. C. H. B.

**Peucedanin and Oreoselone.** By ERNST SCHMIDT, AUGUSTA JASSOY, and P. HAENSEL (*Arch. Pharm.*, 1898, 236, 662—692. Compare Jassoy, Abstr., 1890, 1154; Popper, Abstr., 1898, i, 600).—Crude peucedanin has no definite melting point; it is best purified by several extractions with warm ether, when a white, gritty residue is left; when the ethereal solution is mixed with a considerable amount of light

petroleum, filtered, and left for a time, peucedanin is deposited in clusters of slender needles. After this process has been repeated several times, the compound is obtained in very slender, yellowish needles melting at  $99^{\circ}$ . It can be obtained perfectly colourless only by repeated recrystallisation from very dilute solutions; it then forms colourless, transparent prisms or plates, melting sharply at  $109^{\circ}$ . The melting point has been given very differently by different authorities. It is readily soluble in alcohol, ether, chloroform, acetone, sparingly in benzene or cold, light petroleum. Concentrated acids and alkalis decompose it, yielding oreoselone.

Analyses of the pure compound indicate that it has the composition  $C_{15}H_{14}O_4$ , and not  $C_{16}H_{16}O_4$ , and it is to be regarded as the methyl ether of oreoselone, since it contains one methoxy-group. Attempts to prepare peucedanin synthetically from oreoselone have proved unsuccessful.

A chloroform solution of peucedanin readily decolorises a chloroform solution of bromine, and a product is obtained which crystallises from ether in colourless, six-sided plates, melting at  $140-141^{\circ}$ . Bromine does not react so readily with oreoselone, but after chloroform solutions of the two have been allowed to remain for some time, a vigorous action sets in, and the same product, melting at  $140-141^{\circ}$  is obtained, namely, *monobromoreoselone*,  $C_{14}H_{11}BrO_4$ . Both compounds, when treated with nitric acid, yield nitroso-oreoselone crystallising in hexagonal prisms and pyramids, and melting at  $171^{\circ}$ . When reduced with tin and hydrochloric acid, the nitroso-compound yields hydroxylamine and oreoselone, and when treated with dry ammonia at  $100^{\circ}$ , a product is obtained melting at  $156^{\circ}$  (compare Bothe, *J. pr. Chem.*, 1849, 46, 371). Oreoselone yields a *phenylhydrazone*, melting at  $194^{\circ}$ , and crystallising from alcohol in yellow plates; no phenylhydrazone has been obtained from peucedanin.

When treated with acetic anhydride and zinc chloride, peucedanin does not yield an acetyl derivative, whilst oreoselone, when treated with acetic chloride, yields the monacetyl derivative, melting at  $123^{\circ}$  (compare Popper (*loc. cit.*), and Hlasiwetz and Weidel, *Annalen*, 1874, 174, 67).

Oxypeucedanin,  $C_{30}H_{26}O_9$ , obtained when the insoluble residue left in the purification of peucedanin, is dissolved in a small quantity of chloroform, and the solution mixed with an excess of ether, crystallises in colourless, strongly refractive, spindle-shaped crystals, resembling uric acid (compare Erdmann, *J. pr. Chem.*, 1838, 16, 42, and Heut, *Annalen*, 1875, 176, 70).  
J. J. S.

**Cheiranthin, an Active Constituent of the Wallflower.** By MORITZ REEB (*Chem. Centr.*, 1898, ii, 1102; from *Arch. exp. Path. Pharm.*, 41, 302-308).—Cheiranthin is obtained by evaporating the alcoholic or aqueous extract of the leaves or seeds of the wallflower, removing the inactive oils by light petroleum, treating with lead acetate, and finally salting out the glucoside with magnesium, sodium or ammonium sulphate, when it separates in small, yellow flakes, from which the salts may be removed by means of alcohol and ether. It may also be precipitated by tannin, and in either case still contains an

active alkaloid which may be removed by shaking with ether or ethylic acetate. Chieranthin brings about the characteristic systolic rest in frogs. E. W. W.

**Aspidium spinulosum.** By E. POULSSON (*Chem. Centr.*, 1898, ii, 1103—1104; from *Arch. exp. Path. Pharm.*, **41**, 246—264).—The ethereal extract of the root of *Aspidium* or *Polystichum spinulosum* is evaporated, the residue ground up with calcined magnesia and extracted with water. The flesh-coloured precipitate obtained by adding sulphuric acid to the aqueous solution is dissolved in ether, and the ethereal solution dried over calcium chloride, when it yields a crystalline mass from which, by fractional crystallisation from alcohol, five different compounds may be separated. They are all insoluble in water, more or less soluble in ether, ethylic acetate, benzene, toluene, chloroform, and acetone, very slightly soluble in cold, but very soluble in warm methylic or ethylic alcohol, easily soluble in alkalis, and very slightly in alkaline carbonates; their alcoholic solutions are coloured red or brown by ferric chloride, and their solutions in concentrated sulphuric acid, on warming, become red, and acquire the odour of butyric acid. Their physiological action is like that of filicin.

Polystichin,  $C_{22}H_{24}O_9$  (compare *Arch. exp. Path. Pharm.*, **35**, 97), in alcoholic solution has a feeble acid action on litmus, gives an intense garnet-red coloration with ferric chloride, reduces ammoniacal silver solution, but has no action on Fehling's solution. *Polystichin-aniline*,  $C_{22}H_{24}O_9 \cdot C_6H_7N$ , forms rhombic crystals and melts at  $132^\circ$ .

Polystichalbin,  $C_{22}H_{26}O_9$ , melts at  $150$ — $150.5^\circ$ , crystallises from acetone in small needles spherically arranged, and from alcohol in small, white needles. The alcoholic solution has an acid reaction, and gives a brownish-yellow coloration with ferric chloride. The compound with aniline,  $C_{22}H_{26}O_9 \cdot 2C_6H_7N$ , melts at  $175^\circ$ , that with phenylhydrazine,  $C_{22}H_{26}O_9 \cdot 2C_6H_8N_2$ , separates from alcohol in small, yellow crystals, and melts at  $179^\circ$ . Polystichinin,  $C_{18}H_{22}O_8$ , crystallises from acetone in lustrous, colourless plates, and from ethylic acetate in plates 2—3 cm. long and 0.5 cm. broad; it dissolves in dilute sodium carbonate solution without liberating gas, and the solution becomes deep Burgundy red after several hours. It reduces ammoniacal silver solutions in the cold, but Fehling's solution only on prolonged boiling. The alcoholic solution is feebly acid, and with ferric chloride gives a dark brown coloration. *Polystichocitrin*,  $C_{15}H_{22}O_9$ , crystallises from methylic alcohol in small, lustrous, yellow leaflets, and from alcohol in matted needles; its alcoholic solution is neutral to litmus, and with ferric chloride gives a brownish coloration; its compound with aniline,  $C_{15}H_{22}O_9 \cdot C_6H_7N$ , forms small, yellow prisms and melts at  $117$ — $118^\circ$ . *Polystichoflavin*,  $C_{24}H_{30}O_{11}$ , which crystallises in long, yellow needles often grouped in star-shaped clusters, melts at  $158$ — $158.5^\circ$ ; the alcoholic solution is acid to litmus, and is coloured brown by ferric chloride.

By the action of dilute sodium hydroxide solution and zinc dust on polystichin, polystichic acid, polystichinol, a phenol which melts at  $120$ — $121^\circ$ , and butyric acid are formed. Polystichic acid (*Abstr.*, 1896, i, 387) separates from alcohol in small, lustrous crystals, is very soluble

in alcohol, rather soluble in hot water, dissolves in sodium carbonate solution without liberating carbonic anhydride, has a strong acid reaction, gives a faint yellowish-brown with ferric chloride, and a yellow coloration with aniline; its solution in warm concentrated sulphuric acid has the odour of butyric acid. *Polystichinol*,  $C_{21}H_{30}O_9$ , crystallises from ether in yellow prisms, and from alcohol in slender, pale yellow needles; it melts at  $156.7^\circ$ , is very slightly soluble in cold ether, but easily so in hot ether and in benzene; its alcoholic solution is acid to litmus, and gives a reddish-brown coloration with ferric chloride. In doses of 10 milligrams, polystichic acid and polystichinol have no action on frogs. E. W. W.

**Cantharidin.** II. **Isomerides of Cantharidin.** By HANS MEYER (*Monatsh.*, 1898, 19, 707—726. Compare Abstr., 1898, i, 43).—Cantharic acid, prepared by the action of chlorosulphonic acid on cantharidin, has the molecular weight corresponding with that required for the formula  $C_{10}H_{12}O_4$ , as determined by the boiling point method, using acetone as solvent. The existence of a stable  $\gamma$ -lactone ring in cantharic acid is shown by the fact that, whereas only one equivalent of potash is required to neutralise the acid in the cold, 50 per cent. more is required when the acid is boiled with aqueous potash, a certain proportion of the dipotassium salt being then present in solution. The amount of hydrogen sulphide liberated from a solution of potassium hydrosulphide is also nearly double that calculated for one carboxyl group. Cantharic acid, unlike cantharidic acid, is readily oxidised by alkaline potassium permanganate, but the products of the reaction have not yet been identified. These reactions agree with the constitution

$$\begin{array}{c} C_7H_{10} \\ \diagup \quad \diagdown \\ CO \cdot O \end{array} > CH \cdot COOH.$$

Isocantharidin,  $C_7H_{10} < \begin{array}{c} CH(OH) \\ \diagup \quad \diagdown \\ CO \quad O \end{array} > CO$ , which was obtained by Anderlini and Ghio (Abstr., 1891, 1243), has the same molecular weight as cantharidin, and requires 2 mols. of potash for its neutralisation in boiling solution. When boiled with barium acetate, a barium isocantharidate is produced which, when decomposed by sulphuric acid, yields isocantharidic acid,  $COOH \cdot C_7H_{10} \cdot CH(OH) \cdot COOH$ ; this has the normal molecular weight and is not converted into an anhydride by adding acetic anhydride to its solution in aqueous sodium carbonate, a reaction which confirms the view that it is a derivative of glutaric acid. Isocantharidic acid must be regarded as a hydrate of cantharic acid, and this view is supported by the fact that it is converted into cantharic acid by long continued boiling with water.

A. H.

**Samandarin.** By EDWIN S. FAUST (*Chem. Centr.*, 1898, ii, 1213—1214; from *Arch. exp. Path. Pharm.*, 41, 229—245).—By extracting 200 earth salamanders (*Salamandra maculosa*) with hot water acidified with acetic acid, treating with lead acetate, and precipitating with phosphotungstic acid, the author obtained a solution containing only a small quantity of Zuleski's samandarin. The solution is alkaline, gives precipitates with several alkaloidal reagents, but does not yield crystalline salts. With auric chloride, it becomes turbid,

and the chloride is reduced on warming; with platinic chloride, it gives an amorphous, reddish-brown, and, with bromine water, a yellowish-white, precipitate soluble in hot water. When evaporated with nitric acid, the solution leaves a yellow stain which, with ammonia, gives a yellowish-red, and with sodium hydroxide solution, a red coloration. Physiologically, samandarin affects the nervous system, acting on the nerve centres in the *medulla oblongata*, especially on that connected with the respiratory organs; it causes convulsions, like picrotoxin, &c., and also tetanic spasms. E. W. W.

**Chemistry of Chlorophyll.** By LEON MARCHLEWSKI (*J. pr. Chem.*, 1899, [ii], 59, 22—29).—A continuation of the controversy with Bode (Abstr., 1898, i, 682). C. F. B.

**Chlorophylls.** By ALEXANDRE ÉTARD (*Ann. Chim. Phys.*, 1898, [vii], 13, 556—574. Compare Abstr., 1895, i, 66, 389; 1897, i, 578, ii, 130, and this vol., i, 46).—This paper contains an account of the method employed in extracting the chlorophylls from lucerne (*Medicago sativa*). The greater portion refers to work already published, and the remainder to general considerations unsuitable for abstraction. G. T. M.

**Brazilin and Hæmatoxylin.** IV. By JOSEF HERZIG (*Monatsh.*, 1898, 19, 738—746. Compare Abstr., 1893, i, 426; 1894, i, 341; 1896, i, 379).—Carefully purified brazilin yields both resorcinol and protocathechuic acid on fusion with potash, and must therefore be a derivative of  $\beta$ -resorcylic acid. The fact that the colour of alkaline solutions of brazilin is not due to this substance, is proved by the observation that an alkaline solution which has been rendered perfectly colourless by reduction with hydroxylamine, still yields pure brazilin on acidification. The colour usually seen is due to brazilein. Dimethylbrazilein could only be obtained as a syrup insoluble in alkalis; its *acetyl* derivative is an amorphous substance melting at 150—155°. Acetylbrazelein appears from its properties to be a true brazilein derivative, and not to belong to the brazilin series, as is supposed by Schall and Dralle (Abstr., 1890, 997). Moreover, the product obtained by reducing brazilein with various reducing agents is not identical with brazilin, although its exact nature has not yet been ascertained. All these facts seem to show that brazilein cannot be the quinone of brazilin (compare also Gilbody and Perkin, Proc., 1899, 15, 27, 75). A. H.

**Lichens and their Characteristic Constituents.** By OSWALD HESSE (*J. pr. Chem.*, 1898, [ii], 58, 465—561. Compare Abstr., 1898, i, 531, 679).—Under each lichen is given the locality where it was found, and the substances obtained from it.

*Thamnolia vermicularis* (Sw.), from the Cavalljoch, Vorarlberg.—Thamnolic acid, melting at 210—211° (Zopf, 202—204°, Abstr., 1893, i, 727).

*Cladonia rangiferina* (L.) *vulgaris* (Schaerer) = *C. rangiferina* (Leighton), from Feuerbach near Stuttgart, and from the Starnberger See.—Atranorin and protocetraric acid.

*C. rangiferina* (L.) *silvatica* (Hoffm.) = *C. silvatica* (Nylander), from

between Schloss Solitude and Leonberg (near Feuerbach?), and from the Starnberger See.—Usnic and protocetraric acids, but not cetraric acid, as Zopf asserts.

*C. Floerkeana* Fr. = *C. bacillaris* Ach., from the neighbourhood of Feuerbach.—Coccellic acid (Abstr., 1895, i, 299; 1898, i, 489).

*Parmelia tiliacea* (Hoffm.) Fr. = *Imbricaria tiliacea* Körber, from Ehingen, and from Brand (Vorarlberg).—Atranorin and lecanoric acid; the latter was mistaken by Zopf for a new substance, and named parmeliatic acid.

*P. fuliginosa* Nylander, from Brand, and from Heiden (Switzerland).—Atranorin and lecanoric acid.

*Physcia pulverulenta* (Schreber) Nyl. (*a*).—*allochroa* (Hoffm.) Th. Fr., from the neighbourhood of Schloss Solitude.—A very small quantity of an acid which was not obtained crystallised.

*P. ciliaris* (L.) D. C. = *Anaptychia ciliaris* Körber, from Schloss Solitude.—Evernic acid, and probably atranorin; it is probable that the former was not originally present in the lichen, but was formed from evernic or ramalic acid under atmospheric influence.

*Umbilicaria pustulata* (L.) Hoffmann = *Gyrophora pustulata* Ach., from Weissenstein near Pforzheim, and from St. Blasien (Black Forest).—Gyrophoric acid,  $C_{18}H_{18}O_7$  (?) (Stenhouse, *Annalen*, 70, 218; Zopf, Abstr., 1898, i, 489); when this is boiled with ethylic alcohol, ethylic orsellate is formed, together with an acid melting at  $163^\circ$ , which gives a violet and yellowish-red coloration with ferric chloride and bleaching-powder solutions respectively, and is not orsellic acid, as Zopf asserts.

*Gyrophora polyphylla* (L.) Fro. = *Umbilicaria polyphylla* Fr.—Umbilicatic acid, melting and decomposing at  $180^\circ$  (Zopf, Abstr., 1898, i, 489).

*Endocarpon minutum* (L.) Ach., (*a*) *vulgare* Körber, and ( *$\beta$* ) *complicatum* (Sw.) Fr., from Brand.—Phytosterol (observed in a lichen for the first time) and an acid which gives a bluish-violet coloration with alcoholic ferric chloride.

*Placodium saxicolum* (Poll.) var. *vulgare* Kbr., from Feuerbach.—Usnic acid and zeorin (Paternò, *Atti R. Accad. Lincei*, 1876, [ii], 3; Zopf, Abstr., 1896, i, 104), but not atranorin, as Zopf asserts. Usnic acid is best separated from atranorin by pounding the mixture with concentrated aqueous potassium hydrogen carbonate, filtering, and extracting the residue with chloroform, which dissolves out the atranorin, leaving the potassium usneate behind. Zeorin melts at  $230$ – $231^\circ$ , and has the molecular formula  $C_{52}H_{88}O_4$ ; when it is boiled with alcohol and a little hydrochloric acid, it yields zeorinin,  $C_{52}H_{84}O_2$ , and an amorphous isomeride, *isozeorin*, more soluble in alcohol; these melt at  $182$ – $184^\circ$  and  $184$ – $185^\circ$  respectively; the former crystallises anhydrous from absolute alcohol, with  $2H_2O$  from aqueous alcohol, and is converted into the isomeride by alcoholic hydrochloric acid.

*Blastenia arenaria*, Massalongo = *Calloposma erythrocarpa* (Pers.) de Not., from Feuerbach.—Phytosterol (?) and *blastenin*, an orange-red substance melting at  $270^\circ$ , soluble in aqueous potassium hydrogen carbonate, and apparently related to nephromin.

*B. arenaria* (Pers.) var. *teicholytum* Ach. = *Calloposma teicholytum*



Ach., from Feuerbach.—Atranorin and an acid apparently identical with gyrophoric acid.

*Lecanora sordida* (Pers.), Th. Fr., var. *glaucoma* (Hoffm.), from Feuerbach.—Atranorin and parellic acid, but neither zeorin, nor sordidic nor usnic acid. Zopf's zeoric acid (Abstr., 1897, i, 436) was probably impure parellic acid.

*L. sordida* (Pers.), Th. Fr., var. *Swartzii* (Ach.), from Feuerbach.—From the ethereal extract, atranorin and thiophanic acid crystallise out on cooling; the latter can be removed by extraction with a dilute aqueous alkali hydrogen carbonate. From the ethereal mother liquor, aqueous potassium hydrogen carbonate extracts roccellic and lecasteric acids, of which the latter is the more soluble in chloroform or acetic acid, and its barium salt the more soluble in water. When the residual ethereal solution is evaporated, atranorin and lecasteric acid remain; the latter can be dissolved out with a little hot alcohol.

*Thiophanic acid*,  $C_{12}H_6O_{12}$ , which crystallises from benzene anhydrous, and from acetic acid with  $1H_2O$ , is yellow and melts at  $242^\circ$ ; it loses carbonic anhydride when fused with caustic potash, but not when boiled with aqueous baryta, does not contain a methoxyl group and does not form an acetyl derivative. It is a dibasic acid; the following salts were analysed:  $C_{12}H_4O_{12}K_2 + 4H_2O$ , yellow;  $C_{12}H_4O_{12}Ba + 5H_2O$ , yellow;  $C_{12}H_4O_{12}Pb + H_2O$  (dried at  $110^\circ$ ). When the acid is boiled with hydriodic acid of sp. gr. = 1.7, yellow *thiophaninic acid*,  $C_{12}H_6O_9 + H_2O$ , melting at about  $264^\circ$ , is formed. *Lecasteride*,  $C_{10}H_{18}O_3$ , melts at  $105^\circ$ ; it is converted into lecasteric acid by alkalis and alkali carbonates, and is formed when that acid is boiled with acetic anhydride. *Lecasteric acid*,  $C_{10}H_{20}O_4$ , melts at  $116^\circ$ ; it does not contain methoxyl, and is a monobasic acid; the anhydrous *barium*, *silver*, and *ethylic* salts were analysed. Rocccllic acid melted at  $127-128^\circ$ ; the *barium* salt,  $C_{17}H_{30}O_4Ba$ , was analysed.

*Urceolaria scruposa* (L.), var. *vulgaris* Körber, from Feuerbach.—Atranorin and lecanoric acid.

*U. cretacea* Massalongo = *U. scruposa*, var. *gypsacea* Körber, from Brand.—Lecanoric acid alone, but not atranorin, zeorin, or parmeliac acid, as Zopf asserts (Abstr., 1897, i, 436).

*Pertusaria communis* (DC.)  $\beta$ -*variolosa* Wallr. = *P. amara* = *Variolaria amara*, from Feuerbach and Schloss Solitude.—From the ethereal extract, potassium hydrogen carbonate solution removes cetraric and pertusaric acids; these can be separated by means of the greater solubility of the latter in dilute alcohol. The residual ethereal solution yields a crystalline residue, which is washed with warm alcohol to remove the resinous mother liquor, and then crystallised from hot chloroform, when pertusarin remains dissolved on cooling, whilst pertusarene and pertusaridin separate; of these, the former can be separated by adding light petroleum to a solution of the mixture in hot chloroform. *Pertusaric acid*,  $C_{24}H_{38}O_6$  (or  $C_{23}H_{36}O_6$ ), melts at  $103^\circ$ , and has no bitter taste when pure; the *silver* salt,  $C_{24}H_{37}O_6Ag$ , was analysed. *Pertusarin*,  $C_{30}H_{50}O_2$ , melts at  $235^\circ$ , *pertusarene*,  $C_{60}H_{100}$ , at  $286^\circ$ ; and *pertusaridin*, which has some resemblance to caperidin, at  $242^\circ$ . None of these substances gives a coloration with ferric chloride or bleaching powder. No picrolichenin could be

detected; perhaps the substance described under this name (Alms, *Annalen*, 1, 61; Vogel, *J. pr. Chem.*, [i], 72, 272) was impure per-tusaric acid.

*Thallœdema candidum* (Webr.) Körber, from Brand.—Traces of an acid, perhaps lecanoric acid.

*Baeomyces roseus* (Pers.) from Stockheim (Wurtemberg) and Brand.—In addition to wax, it contains an acid which melts at about 180° and gives a violet coloration with ferric chloride.

*Lecidea cinereoatra* Ach., from Brand.—From the ethereal extract, potassium hydrogen carbonate solution removes lecidic acid and lecidol, which can be separated by means of the greater solubility of the latter in dilute alcohol. *Lecidic acid*,  $C_{22}H_{27}O_4 \cdot COOMe$ , melts at 147°, and contains either one or two COOH groups in addition to the COOMe group. *Lecidol*, melts at 93°, and has the character of a phenol; the pure substance is not soluble in potassium hydrogen carbonate solution.

*Rhizocarpon geographicum* (L.) DC. *f. lecanorinum* (Flörke) and *f. geronticum* Ach., from Baden, the Luisenberg and the Arber (Böhmerwald), the Achensee (Tyrol), and Brand.—From the ethereal solution, aqueous potassium hydrogen carbonate extracts parellic acid: also, rhizocarpic acid, in the case of the lichen from the Luisenberg and probably in the other cases; the latter acid is extracted from the mixture by cold alcohol. The residual ethereal solution yields rhizocarpic acid when evaporated. *Rhizocarpic acid*,  $COOH \cdot C_{24}H_{16}O_3 \cdot COOEt$ , is yellow, and melts at 177—178°; its potassium salt, with  $1H_2O$ , is yellow, and insoluble in aqueous potassium hydrogen carbonate; when it is evaporated repeatedly with potassium carbonate, it yields *nor-rhizocarpic acid*,  $C_{24}H_{16}O_3(COOH)_2$ ; this acid is yellow and melts at 92°; the potassium salt, with  $5H_2O$ , is also yellow; and so is the *diethylic* salt, which is obtained by boiling rhizocarpic acid with alcohol and a little hydrochloric acid, and melts at 159°. When rhizocarpic acid is warmed for 6 hours with acetic anhydride at 85° and the mixture evaporated, a yellow *monacetyl* derivative, melting at 168°, is obtained; if it is boiled with the anhydride, pulvic anhydride is formed; some ethylpulvic acid is formed when it is boiled for a short time with aqueous baryta. *Rhizocarpic acid* is yellow and melts at 156°. Parellic acid (identical with Zopf's psoromic acid, *Abstr.*, 1895, i, 298; 1897, i, 363; and the squamaric, and, probably, zeoric acid of other writers),  $COOMe \cdot C_{17}H_{11}O_3(COOH)_2$ , crystallises from glacial acetic acid with  $3H_2O$ , from moderately dilute alcohol with  $1H_2O$ ; the anhydrous acid melts and decomposes at 262—265°. It is a dibasic acid, and contains one methoxyl group; it yields neither an ethylic salt nor an acetyl derivative; the following salts were analysed,  $2C_{21}H_{14}O_9Pb \cdot PbO$  (with  $H_2O$  in addition, if dried in a desiccator only);  $C_{21}H_{14}O_9Ag_2$ ;  $C_{21}H_{15}O_9Ag$ . When the acid is boiled with aqueous baryta or potassium carbonate, it loses carbonic anhydride and methylic alcohol, and yields *parellinic acid*,  $C_{17}H_{14}O_4(COOH)_2$ , which melts and decomposes at 230°; it is a dibasic acid; the yellow barium salt, with  $6H_2O$ , was analysed.

*Rhizocarpon geographicum* (L.) DC. *f. contiguum* Fr., from Brand.—When the ethereal extract was shaken with potassium hydrogen

carbonate solution, the potassium salts of parellic and rhizonic acids separate out, whilst rhizocarpic acid remains dissolved; of the two salts, the first dissolves in cold water, the latter does not (perhaps it could be used for the separation of potassium and sodium, as the sodium salt is soluble in water). Calcium oxalate is also present in the lichen. *Rhizonic acid*,  $\text{OMe} \cdot \text{C}_{17}\text{H}_{14}\text{O}_2(\text{OH})_2 \cdot \text{COOH}$ , melts and decomposes at  $185^\circ$ ; the *barium*, with  $3\text{H}_2\text{O}$ , *copper*, with 3 or  $4\text{H}_2\text{O}$ , and anhydrous *potassium*, *calcium*, *lead*, and *silver* salts were analysed. When it is heated with hydriodic acid, betorcinol is formed, together with methylic iodide and carbonic anhydride; the same products are also obtained when the acid is boiled with aqueous baryta, but some *rhizoninic acid*,  $\text{OMe} \cdot \text{C}_6\text{HMe}_2(\text{OH}) \cdot \text{COOH}$ , is also formed; this melts at  $186^\circ$ , and, like rhizonic acid, yields betorcinol, methylic iodide and carbonic anhydride, when it is heated with concentrated hydriodic acid; its *potassium*, with  $1\text{H}_2\text{O}$ , *barium*, with  $3\text{H}_2\text{O}$ , and *copper*, with  $3\text{H}_2\text{O}$ , salts were analysed, and a crystalline *ethylic* salt was prepared. Rhizonic acid is a lactonic acid; it is related to rhizoninic acid in the same way as evernic to everninic acids, and the first pair is derived from betorcinol in the same way as the second pair from orcinol.

*Calycium chrysocephalum* Ach. = *Cypheium chrysocephalum*, Ach., from Feuerbach and Munich.—Vulpic acid only.

*Cypheium trichiale* f. *candelare*, Arnold, from Munich.—Calycin.

*Lepra candelaris* Schaerer = *Lepraria flava* Acharius, from Feuerbach, the Black Forest, Salzburg, and on cinchona bark from Bolivia, India, Ceylon, and Java.—Calycin,  $\text{C}_{18}\text{H}_{11}\text{O}_4 \cdot \text{OH}$ , melts at  $240\text{--}242^\circ$ ; it yields a purple-red *potassium* derivative, with  $2\text{H}_2\text{O}$ , when treated with alcoholic potash or concentrated aqueous potassium carbonate; this decomposes into calycin and potassium calcate,  $\text{C}_{18}\text{H}_{12}\text{O}_6\text{K}_2$ , when it is boiled with water. When calycin is heated for several hours at  $100^\circ$  with caustic potash of sp. gr. =  $1.15^\circ$ , crystals are obtained which melt at  $195^\circ$ , and are possibly oxatoluic acid. When 40 per cent. potash is used and the heating continued for 1 hour at  $100^\circ$  and then for 1 hour at  $150^\circ$ , the products are oxalic and  $\alpha$ -toluic acids, with possibly a little toluene. Calycin yields a yellow *acetyl* derivative, melting at  $178^\circ$ . It was not found possible to convert calycin into vulpic (methylpulvic) acid, although it is undoubtedly related to pulvic acid.

*Pulveraria chlorina* Ach. = *Lepra chlorina* Stenh., from St. Anton (Tyrol).—Calycin remains in the ethereal extract, whilst potassium hydrogen carbonate removes vulpic and lepraric acids from the ether; these were separated by crystallisation from acetone. *Lepraric acid* melts at  $228^\circ$ , and does not give any coloration with ferric chloride or bleaching powder.

*P. latebrarum* = *Lepra latebrarum* Ach., from Brand.—From the ethereal extract, atranorin separates on cooling. Potassium hydrogen carbonate solution removes parellic acid. The residual ethereal solution yields atranorin, latebride, and pulverin; of these, the last two can be dissolved out with dilute alcohol and separated by means of the greater solubility of latebride in chloroform. *Latebride* melts at  $128^\circ$ ; it forms, with concentrated potash, a gelatinous precipitate, but this dissolves after a time, and an acid, *latebraric acid*, can then be

isolated from the solution. *Pulverin* is pale yellow ; it melts and decomposes at  $262^{\circ}$ .

*P. farinosa* Ach.—From the ethereal extract, potassium hydrogen carbonate removes oxyroccellic and pulveraric acids ; the first of these forms an insoluble, the latter a soluble barium salt. *Pulveraric acid* melts at  $234^{\circ}$ , and gives a blue coloration with ferric chloride.

*Cetraria islandica* (L.) Ach. (compare Abstr., 1898, i, 534, and Sinnhold, this vol., i, 13).—Samples purchased from Frankfort and Stuttgart, and one collected near Wunsiedel (Fichtelgebirge) contain a lichenostearic acid, or acids, with melting points ranging between  $109-120^{\circ}$ , and composition between C 69.1—70.0, H 9.5—9.9. From a second sample purchased from Frankfort, a small quantity of another acid, *paralichenostearic acid*, was isolated in addition ; this melts at  $183^{\circ}$ , and has the composition C 67.6, H 10.0.

As regards the occurrence, in lichens generally, of the substances described, it cannot be said that a particular constituent is characteristic of a particular lichen ; it often occurs in other, and by no means closely related, lichens as well. The season of the year has some, but not a great influence in determining what constituents are present : *Cladonia rangiferina* var. *silvatica* contains fatty acids in summer, but not in winter. The nature of the material upon which the lichen grows has more influence : *Parmelia caperata* contains caperin and caperidin when it has grown on oaks, but not when it has grown on fruit trees or on granite ; and *Xanthoria parietina* usually contains physcion, but this is absent when the lichen has grown on pines, and atranorin is present instead, and the colour is now greenish instead of yellow. Climate has a great influence : *Parmelia perlata* from Germany contains atranorin only, whereas that from America contains vulpic and usnic acids, and that from India perlatin and lecanoric acid, in addition. The use of chemical tests to distinguish species of lichens is not admissible, as different parts of the same lichen may react differently. C. F. B.

**Constitution of Indican and of some Derivatives of Indigotin.** By LEON MARCHLEWSKI and L. G. RADCLIFFE (*J. Soc. Chem. Ind.*, 1898, 17, 430—434).—The constitution suggested for glucosides

(Abstr., 1894, i, 104), namely,  $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}\cdot\text{CH}\cdot\text{OR}$ , in

which R represents a phenolic or basic residue, is considered preferable to the one previously suggested (*Trans.*, 1893, 1137). Acetochlorhydrose is constituted in much the same manner as a glucoside, and should therefore be either  $\text{OAc}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CH}\cdot\text{CH}\cdot\text{OAc}$ , or  $\text{OAc}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OAc}]_3\cdot\text{CH}\cdot\text{CH}\cdot\text{OAc}$ . As galactose cannot be found

among the products of hydrolysis, the second formula is considered the more probable.

In view of Schunck and Römer's work (*Ber.*, 1879, 12, 2311), indican cannot be regarded as the glucoside of indigo white ; it cannot contain the whole indigotin molecule in any form, and indigotin is produced by condensation going on under favourable conditions simul-

taneously with the hydrolysis of indican. The constitution now suggested for indigotin,  $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_3 \cdot \text{CH} < \begin{smallmatrix} \text{CH} \cdot \text{O} \cdot \text{C} \cdot \text{CH} \\ \text{O} \qquad \text{C}_6\text{H}_4 \end{smallmatrix} > \text{NH}$ , represents it as the glucoside of indoxyl.

The acid obtained by O'Neill (Abstr., 1892, 991) on oxidising indigo suspended in glacial acetic acid and hydrolysing the product, is shown to have the composition  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_6$ , when air dried, and is termed *di-isatic acid*; it contains water of crystallisation, softens at  $140-149^\circ$ , but melts at  $226-227^\circ$ . When dried at  $110-115^\circ$  it loses  $2\text{H}_2\text{O}$ , yielding an anhydrous acid, *di-isatin*,  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4$ ; this is a white powder readily soluble in methylic or ethylic alcohol, or acetone, but insoluble in chloroform, carbon bisulphide, or ether. Titration with standard alkali indicates that the composition of its *sodium* salt is  $\text{C}_{16}\text{H}_9\text{NaN}_2\text{O}_4$ , and that of the hydrated acid  $\text{C}_{16}\text{H}_{13}\text{NaN}_2\text{O}_6$ . A bromo-derivative of the hydrated acid, namely,  $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_6$ , has been obtained as a white powder which slowly melts and decomposes.

From a study of the behaviour of natural and artificial indigos on oxidation, it would seem that the two are identical; indirubin, on the other hand, differs from indigo on oxidation. Although indirubin is readily reduced to indigotin in the presence of acid reducing agents, the reduction does not proceed so readily when alkaline reducing agents are employed.

J. J. S.

**Action of Ethylenic Iodide on Pyridine.** By ALBERT LADENBURG (*Ber.*, 1899, 32, 42-46. Compare Abstr., 1883, 1151).—Pyridine (5.5 grams) was heated with di-iodethane (16 grams) and absolute alcohol (about 2 grams) at  $310-320^\circ$  for 10 hours, the operation being repeated 180 times in all, and the united product submitted to repeated fractional distillation; the products were (a) pyridine, boiling at  $115-120^\circ$ ; (b) 2-ethylpyridine, boiling at  $146-153^\circ$ , and yielding picolinic acid on oxidation (the *mercurochloride*,  $\text{C}_5\text{NH}_4\text{Et} \cdot \text{HCl} \cdot 2\text{HgCl}_2$ , melts at  $103-106^\circ$ ); and (c) 4-ethylpyridine, boiling at  $160-168^\circ$ , and giving isonicotinic acid when oxidised. Probably the ethylenic iodide does not act directly on the pyridine, but decomposes, yielding hydrogen iodide, which then reacts with the alcohol present to form ethylic iodide, the ethylpyridines being produced by the action of the pyridine on the latter.

C. F. B.

**New Organo-metallic compounds.** By FRITZ BLAU (*Monatsh.*, 1898, 19, 647-689).—*aa*-Dipyridyl combines with ferrous salts, forming stable, deep red tridipyridylferrous salts of the general formula  $(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{FeR}_2$ ; these are characterised by specific reactions entirely different from those of ferrous salts, and are only very slowly decomposed by acids and by ammonium sulphide. The soluble compounds dye silk and wool pink. *Tridipyridylferrous sulphate*, formed when dipyridyl is added to an aqueous solution of ferrous sulphate, is a deep red, crystalline mass which is extremely soluble in water. The other salts are best prepared from this compound by double decomposition; the sulphate and nitrate are readily soluble, the chloride, bromide, and iodide less readily, and the others insoluble, or sparingly soluble, in water. The *iodide*, with  $5\text{H}_2\text{O}$  or  $8\text{H}_2\text{O}$ , and the

*bromide* crystallise in dark-red, lustrous, six-sided tablets; the *platinochloride*,  $(C_{10}H_8N_2)_3FePtCl_6 + 5\frac{1}{2}H_2O$ , forms brownish-red, crystalline aggregates. The *base*,  $(C_{10}H_8N_2)_3Fe(OH)_2$  is formed when baryta is added to the sulphate, and is a red, strongly alkaline substance which combines with atmospheric carbonic anhydride, and readily decomposes, forming ferric hydroxide. The formation of these compounds proceeds even in acid solution, and the coloration which is produced may be used as a test for dipyrindyl. Similar compounds are formed with salts of zinc, cadmium, nickel, cobalt, and copper, but not with salts of the alkali metals, alkaline earth metals, lead, manganese or aluminium. The red salts are not affected by atmospheric oxygen, or by oxidising agents of moderate strength, but are converted by potassium permanganate, nitric acid, and chlorine water, into *tridipyrindylpseudo ferric salts*,  $(C_{10}H_8N_2)_3FeR_3$  which form blue solutions in water; these compounds are not formed when dipyrindyl is added to ferric salts. They are very readily reconverted into the original red salts by reducing agents, such as hydrogen sulphide, metallic silver, hydrobromic acid, hydrogen peroxide, and also by exposure to light. Acids do not cause decomposition when the possibility of reduction is excluded; alkalis render the blue solutions red, a smell of ozone being produced, but on acidifying, the blue colour returns. The *sulphate* has not been obtained in the pure state, but the *platinochloride* is a well characterised compound,  $(C_{10}H_8N_2)_6Fe_2(PtCl_6)_3$ , which crystallises with 19 or  $20H_2O$ , in slender, green needles, the anhydrous compound being brown.

Tridipyrindylnickel salts, which are formed in a similar manner to the ferrous salts, are pink; the *bromide*,  $(C_{10}H_8N_2)_3NiBr_2 + 6\frac{1}{2}H_2O$ , crystallises in six-sided tablets, and the other salts resemble it in appearance. Tridipyrindylcobalt salts form brownish-yellow solutions; the *bromide* crystallises in yellow, six-sided tablets, and dissolves in about 100 parts of water. Two series of copper salts are known, produced by the union of 1 mol. of copper salt with 1 or 2 mols. of the base. *Dipyrindylcopper sulphate*,  $C_{10}H_8N_2 \cdot CuSO_4 + 2H_2O$ , crystallises in sparingly soluble, blue needles, and the *chloride* forms compact green crystals readily soluble in water; the compounds containing 2 mols. of the base are very unstable. Dipyrindyl also forms colourless compounds with the salts of zinc and cadmium; these are sparingly soluble in water. Compounds also seem to be formed with chromic and ferric salts, but no definite results have as yet been obtained.

The isomerides of *aa*-dipyrindyl do not form similar compounds, and in this respect resemble aniline, naphthylamine, the phenylenediamines, benzidine, &c. One or two direct derivatives of *aa*-dipyrindyl, however, behave somewhat similarly, and a series of similar compounds has been obtained from the  *$\alpha$ -phenanthroline* prepared from orthophenylenediamine; this compound crystallises with  $1H_2O$  in vitreous, hexagonal plates melting at  $102^\circ$ , whilst the anhydrous compound melts at  $117^\circ$ . The *platinochloride* crystallises in microscopic prisms, and the *dichromate* in sparingly soluble needles; the metallic compounds of this base closely resemble those of dipyrindyl in almost every respect. *Triphenanthrolineferrous sulphate*, prepared by adding the base to ferrous sulphate solution, serves as a source of the

other compounds; the *bromide*,  $(C_{12}H_8N_2)_3FeBr_2 + 7H_2O$  crystallises in red, quadratic prisms. The ferrous salts are converted by oxidation into blue pseudo-ferric compounds; *triphenanthrolinepseudo-ferric platinochloride*,  $(C_{12}H_8N_2)_6Fe_2(PtCl_6)_3$ , crystallises in green needles, which yield an olive-green residue of anhydrous salt when dried over sulphuric acid. *Triphenanthroline-nickel bromide* forms pink tablets, whilst the corresponding *cobalt* compound crystallises in yellow needles. The compounds with copper, zinc, and cadmium salts, closely resemble those of dipyridyl.

The constitution of these compounds appears to be best explained by Werner's theory of the metalammines, according to which they must be classed as hexammines (luteo-salts), all the acid radicles being capable of entering into double decompositions. A. H.

**A Di-iodoquinoline.** By CONSTANTIN I. ISTRATI (*Compt. rend.*, 1898, 127, 520—521).—The method employed by the author for the iodation of benzene and its chlorine derivatives, and for the preparation of franceines, which consists in prolonged heating of the substance with concentrated sulphuric acid and iodine, is found to be generally applicable to cyclic nitrogen compounds. In the case of quinoline, much sulphurous anhydride is evolved, the mixture thickens and becomes of a reddish-brown or black colour, and on pouring the mass into water a precipitate is produced which consists of iodoquinolines and iodo-franceines, whilst moniodoquinoline, sulphonic derivatives, and unaltered quinoline remain in solution. By treating the precipitate with potash, filtering, and exhausting the insoluble residue with alcohol, a *di-iodoquinoline*,  $C_9NH_5I_2$ , is obtained, which forms yellowish-brown crystals melting at  $164-165^\circ$ . It is very soluble in alcohol and chloroform, and forms a yellow *platinochloride* and other salts, which are decomposed by excess of water. The moniodoquinoline crystallises from alcohol in small, colourless needles melting at  $101-102^\circ$ , and is, perhaps, identical with the 5-iodoquinoline described by Claus and Grau (*Abstr.*, 1893, i, 669) as melting at  $100^\circ$ . Its platinochloride, however, does not melt and decompose at  $263^\circ$ , as stated by those observers, and is separable by treatment with hot water, into two portions: the one, soluble in water, crystallises in orange-yellow needles, which lose iodine at  $210^\circ$ , and melt and decompose at  $228^\circ$ , whilst the other, insoluble in water, is of a golden-yellow colour, and melts and decomposes at  $230-260^\circ$ . N. L.

**Condensation Products of Formaldehyde with Quinaldine.** By WILHELM KOENIGS (*Ber.*, 1899, 32, 223—231. Compare this vol., i, 74).—Quinaldine combines not only with 1 mol. of formaldehyde, as Methner has stated, but also with 2 and 3 mols., forming  $\alpha$ -quinolylpropanediol and  $\alpha$ -quinolylbutanetriol, respectively.

$\alpha$ -Quinolylethanol [2-hydroxyethylquinoline],  $C_9NH_6 \cdot CH_2 \cdot CH_2 \cdot OH$ , which was described under the name of quinaldinealkin by Methner (*Abstr.*, 1895, i, 71), crystallises from ethylic acetate in colourless, hexagonal plates melting at  $104-105^\circ$  ( $94-95^\circ$  Methner); the *picrate* crystallises from water in yellow needles melting and decomposing at  $165^\circ$ , the aurichloride forms glistening, yellow scales melting at  $132-135^\circ$ , and the platinochloride separates from hot dilute

hydrochloric acid in yellowish-red plates melting and decomposing at  $210^{\circ}$ .

$\alpha$ -Quinolylpropanediol,  $C_9NH_6 \cdot CH(CH_2 \cdot OH)_2$ , formed by heating a mixture of quinaldine and formaldehyde in a sealed tube for 40 hours in a water-bath, crystallises from ethylic acetate or from hot water in colourless prisms which melt at  $116-117^{\circ}$ , and are readily soluble in ethylic and methylic alcohol, methylal, acetone, and chloroform, sparingly in cold ethylic acetate and in benzene, and almost insoluble in ether, carbon bisulphide, and light petroleum; the *picrate* melts at  $146-147^{\circ}$ ; the *aurichloride*, when first formed, is an oil, but solidifies on standing, and the *platinochloride*, after drying at  $130^{\circ}$ , melts and decomposes at  $155-160^{\circ}$ .  $\alpha$ -Quinolylpropanediol, on reduction with phosphorus and hydriodic acid, yields 2'-isopropylquinoline, which is identical in every respect with the compound obtained by Doebner (Abstr., 1887, i, 504) from  $\alpha$ -isopropylcinchonic acid, and yields an *aurichloride* melting at  $124-126^{\circ}$ , and a *platinochloride* melting at  $194^{\circ}$ .

$\alpha$ -Quinolylbutanetriol,  $C_9NH_6 \cdot C(CH_2 \cdot OH)_3$ , formed from quinaldine and 3 mols. of formaldehyde, crystallises from ethylic acetate or benzene, and melts at  $143^{\circ}$ ; the *hydrochloride* melts at  $143-146^{\circ}$ , the *platinochloride* is readily soluble, and the *aurichloride*, which crystallises in glistening, yellow leaflets containing  $1H_2O$ , melts at  $86^{\circ}$ , or when anhydrous, at  $122-123^{\circ}$ ; on oxidation with nitric acid, the base yields quinoline-2'-carboxylic acid, and on reduction with phosphorus and hydriodic acid, not tertiarybutylquinoline, but  $\alpha$ -isopropylquinoline, which seems to point to this compound as being in reality  $\alpha$ -quinolylpropanediol containing formaldehyde of crystallisation; the author is disinclined to this belief, however, owing to the fact that not only does  $\alpha$ -quinolylbutanetriol yield no compound with phenylhydrazine, but also that  $\alpha$ -quinolylpropanediol may be boiled for a prolonged period with formaldehyde without change; further, the base does not react with Tollen's reagent for formaldehyde. J. F. T.

**Synthesis of Pyridazine and its Derivatives.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1899, 32, 395-409).—When benzoylacrylic acid (von Pechmann, Abstr., 1882, 1074) is warmed with an aqueous solution of hydrazine, it gives rise to the *hydrazone*,  $N_2H_5 \cdot CPh \cdot CH : CH \cdot COOH$ , which separates from absolute alcohol in slender, colourless crystals, melts and decomposes at  $185-186^{\circ}$ , and is not convertible into 3-phenylpyridazine by the loss of  $1H_2O$ . Benzoylpropionic acid, however, like its ethylic and methylic salts (Curtius, Abstr., 1895, i, 246; von Rothenburg, *ibid.*, 302), when acted on by hydrazine, gives rise to phenylpyridazinone,  $\begin{array}{c} CPh \cdot CH_2 \cdot CH_2 \\ | \\ N - NH - CO \end{array}$ ; on dissolving this (70 grams) in glacial acetic acid (200 c.c.) and adding bromine (65 grams), it is converted into a *bromophenylpyridazinone*, which loses hydrogen bromide when crystallised from alcohol, and gives rise to 3-phenylpyridazine,  $\begin{array}{c} CPh \cdot CH : CH \\ | \\ N - NH - CO \end{array}$ , melting at  $201-202^{\circ}$ . On warming the latter with phosphorus oxychloride, it yields 3-phenyl-



6-chloropyridazine,  $\begin{array}{c} \text{CPh} \cdot \text{CH} : \text{CH} \\ | \quad \quad | \\ \text{N} - \text{N} = \text{CCl} \end{array}$ , which crystallises from alcohol in

long, colourless prisms, and melts at  $160^\circ$ ; it is converted by sodium methoxide into 3-phenyl-6-methoxyppyridazine, which crystallises from alcohol in fan-shaped aggregates of needles, melts at  $116-117^\circ$ , and yields well-defined compounds with hydrogen chloride, potassium dichromate, picric acid, and gold and platinum chlorides. On boiling 3-phenyl-6-chloropyridazine for 2 hours with concentrated hydriodic acid (b. p.  $127^\circ$ ) in presence of red phosphorus, it is converted into 3-phenyl-6-iodopyridazine,  $\text{C}_{10}\text{H}_7\text{N}_2\text{I}$ , which crystallises from absolute alcohol in snow-white needles, and, when heated, sinters at  $163^\circ$ , and melts at  $169-170^\circ$ ; when, however, the boiling is continued for 5 hours, 3-phenylpyridazine,  $\begin{array}{c} \text{CPh} \cdot \text{CH} : \text{CH} \\ | \quad \quad | \\ \text{N} - \text{N} = \text{CH} \end{array}$ , is obtained, which crystal-

lises from water or light petroleum in long needles, melts at  $102-103^\circ$ , boils unchanged at  $330-332^\circ$ , sublimes slightly at  $100^\circ$ , and has an odour resembling that of diphenyl. The hydriodide,  $\text{C}_{10}\text{H}_8\text{N}_2\text{HI}$ , forms yellow prisms, and the platinochloride,  $(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{H}_2\text{PtCl}_6$ , very slender needles, whilst the golden-yellow, crystalline aurichloride,  $\text{C}_{10}\text{H}_8\text{N}_2\text{HAuCl}_4$ , melts at  $159^\circ$ , and the picrate at  $127^\circ$ .

When 3-phenylpyridazine is reduced with alcohol and sodium, and the product dissolved in dilute nitric acid, phenylhexahydropyridazine nitrate,  $\begin{array}{c} \text{CHPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{NH} - \text{NH} - \text{CH}_2 \end{array} \text{HNO}_3$ , is obtained, which forms thick, colour-

less needles, and, when heated, sinters at  $179^\circ$ , and melts at  $187^\circ$ ; the base is an oil, whilst the picrate,  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms yellow prisms and melts at  $170-171^\circ$ . On nitration, 3-phenylpyridazine gives rise to a mixture of isomeric nitro-derivatives,  $\text{C}_{10}\text{H}_7\text{N}_3\text{O}_2$ , which seem to crystallise together from water, since the crystals commence to melt at  $151^\circ$  and finally liquefy at  $195^\circ$ ; when reduced, an amido-phenylpyridazine,  $\text{C}_{10}\text{H}_9\text{N}_3$ , is obtained, which crystallises from dilute alcohol in rhombic plates, softens at  $110^\circ$ , melts at  $120-124^\circ$ , and is converted by the diazo-reaction into a hydroxyphenylpyridazine,  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}$ ; this, when heated, softens at  $170^\circ$ , melts at  $177-180^\circ$ , and is not identical with that described below.

Paramethoxybenzoylpropionic acid,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared by adding powdered aluminium chloride (15 grams) to succinic anhydride (10 grams) dissolved in phenetol, crystallises from alcohol in flat, rhombic plates, and melts at  $138-139^\circ$ ; analogy with Nourrisson's results (Abstr., 1886, 1029) in the case of anisoil and phthalic anhydride indicates that the ethoxy-group is in the para-position. When hydrazine sulphate is added to a solution of the acid in excess of caustic soda, paraphenetylpyridazinone,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} - \text{NH} \end{array} \text{CO}$ , is obtained, which forms long needles, and melts at  $145-146^\circ$ . When this is treated with bromine (1 mol.) in glacial acetic acid solution, it gives rise to a monobromo-derivative,  $\text{C}_{12}\text{H}_{11}\text{N}_2\text{BrO}_2$ , which separates in beautiful, transparent rhombs, and melts at  $240-243^\circ$ ; 3-bromophenetyl-6-chloropyridazine,  $\text{OEt} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{C} \begin{array}{c} \text{CH} : \text{CH} \\ \diagup \quad \diagdown \\ \text{N} - \text{N} \end{array} \text{CCl}$ , prepared

from it by the action of phosphorus oxychloride, crystallises from alcohol in colourless needles, melts at 152—153°, and is converted by boiling hydriodic acid (b. p. 127°) into 3-*parahydroxyphenylpyridazine*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} \text{CH}$ , which dissolves sparingly in water, but easily in alcohol. It is readily oxidised by cold aqueous potassium permanganate to *pyridazine-3-carboxylic acid*,  $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ \text{N} \text{---} \text{N} \end{smallmatrix} \text{CH}$ , which crystallises from water in needles or plates, melts at 200—201°, and yields a crystalline *hydrochloride*, *aurichloride*, and *platinochloride*; the *copper salt*,  $(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_2\text{Cu}$ , crystallises from water in bright blue rhombs. Pyridazine, obtained on distilling the carboxylic acid, has a sp. gr. = 1.1108 at 18.1°, referred to water at 16.5°, and possesses the properties ascribed to it by Täuber (Abstr., 1895, i, 301); its *picrate*,  $\text{C}_4\text{H}_4\text{N}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms citron-yellow needles which sinter at 160° and melt and decompose at 175°. W. A. D.

**Synthesis of Pyridazone-derivatives.** By AUGUSTIN BISTRZYCKI and HUGO SIMONIS (*Ber.*, 1899, 32, 534—536).—The aliphatic 1:4-aldehyde-acid, mucobromic acid, like the aromatic orthaldehyde-acids, shows a tendency to pass into ring compounds by the condensation of its side chains.

When mucobromic acid, in alcoholic solution, is boiled with phenylhydrazine, a mixture of the phenylhydrazone and its inner anhydride is formed; this can be separated by means of dilute sodium hydroxide solution.

*Mucobromic acid phenylhydrazone*,  $\text{N}_3\text{HPh} \cdot \text{CH} \cdot \text{CBr} \cdot \text{CBr} \cdot \text{COOH}$ , is difficult to obtain pure, since, on acidifying the sodium hydroxide solution, it does not separate unchanged; crystals which had been mechanically separated from the original mixture melted at 105—110°.

*Phenyldibromopyridazone*,  $\text{CH} \begin{smallmatrix} \text{CBr} \cdot \text{CBr} \\ \text{N} \text{---} \text{NPh} \end{smallmatrix} \text{CO}$ , the inner anhydride, is, however, readily obtained pure, and crystallises from alcohol in glistening, colourless, truncated prisms, melting at 145°; it is insoluble in water, dilute aqueous potash, or diluted mineral acids, but readily soluble in glacial acetic acid or toluene.

*Dibromopyridazone*,  $\text{CH} \begin{smallmatrix} \text{CBr} \cdot \text{CBr} \\ \text{N} \text{---} \text{NH} \end{smallmatrix} \text{CO}$ , separates as a crystalline precipitate when an aqueous solution of mucobromic acid, hydrazine sulphate, and sodium acetate is boiled; it crystallises from alcohol in colourless needles, melting at 224°, and is readily soluble in warm dilute sodium hydroxide solution. On adding baryta to the pyridazone, the *barium salt* separates in white needles containing  $1\frac{1}{2}\text{H}_2\text{O}$ ; this it loses on drying at 110°, becoming at the same time coloured an intense yellow. J. F. T.

**1:9-Dimethyluric Acid and 1:7:9-Trimethyluric Acid.** By EMIL FISCHER and FRIEDRICH ACH (*Ber.*, 1899, 32, 250—260).—The following experiments were undertaken with the object of preparing 1:9-dimethyl- and 1:7:9-trimethyl-uric acid, and thus completing the list of the possible di- and tri-methyl derivatives of uric

acid. 2-Chloro-6-amido-8-oxy-9-methylpurine (Abstr., 1898, i, 280), is converted by nitrous acid into 2-chloro-6:8-dioxy-9-methylpurine,  $\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH}-\text{CO}$ , which crystallises in long matted needles, and melts and decomposes at about  $320^\circ$  (corr.); this, when treated with ammonia, yields the corresponding amido-compound, from which a large amount of guanidine can be obtained on oxidation. Chlorodioxy-methylpurine, on reduction with hydriodic acid and phosphonium iodide at  $60^\circ$ , yields 6:8-dioxy-9-methylpurine,  $\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NH}-\text{CO}$ , which

crystallises from hot alcohol in short, compact prisms, and becomes brown at  $390^\circ$  without melting. Chlorodioxy-9-methylpurine readily reacts with methylic iodide in alkaline solution, forming 2-chloro-6:8-dioxy-1:7:9-trimethylpurine,  $\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Cl}$ , which crystallises in slender needles melting at  $258-259^\circ$  (corr.). The chlorodioxy-9-methylpurine is converted by a smaller amount of methylic iodide into

2-chloro-6:8-dioxy-7:9-dimethylpurine,  $\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{NMe}-\text{CO}$ , which is also formed by the action of dilute alkalis on 2:6-dichloro-8-oxy-7:9-dimethylpurine; it separates from acetic acid in granular crystals and melts at  $312^\circ$  (corr.). 2-Chloro-6:8-dioxy-1:7:9-trimethylpurine is readily converted by heating with hydrochloric acid into

1:7:9-trimethyluric acid,  $\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{NMe}-\text{CO}$ , which crystallises from alcohol or water in lustrous needles and melts and decomposes at  $348^\circ$  (corr.); this acid closely resembles hydroxycaffeine in its properties, but is less stable than the latter, and does not give so marked a murexide reaction. The silver salt crystallises in slender, matted needles soluble in ammonia.

2-Chloro-6:8-dioxy-1:9-dimethylpurine is prepared by acting on 2-chloro-6:8-dioxy-9-methylpurine with formaldehyde, treating the potassium salt of the hydroxymethyl derivative thus formed with methylic iodide, and hydrolysing the product. It crystallises in lustrous needles and melts and decomposes at  $291^\circ$  (corr.). This compound is converted by reduction into 6:8-dioxy-1:9-dimethylpurine, which forms concentric groups of small needles, and melts at  $360-362^\circ$  (corr.). When heated with hydrochloric acid, it yields 1:9

dimethyluric acid,  $\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{NH}-\text{CO}$ , which crystallises in rectangular tablets, is soluble in 360 parts of boiling water, decomposes at about  $400^\circ$ , and reduces ammoniacal silver oxide solution when boiled with it. The sodium salt is precipitated by concentrated aqueous soda in fascicular groups of needles; the potassium salt crystallises in very slender needles. A. H.

**The Purine group.** By EMIL FISCHER (Ber., 1899, 32, 267-273).—When treated with alcoholic ammonia at  $100^\circ$ , trichloro-9-methylpurine is converted into dichloro-9-methyladenine, and a compound  $\text{C}_6\text{H}_5\text{N}_5\text{Cl}_2$ , which melts and decomposes at  $314^\circ$ , and is probably the isomeric 2:6-dichloro-8-amido-9-methylpurine.

The  $\alpha$ -dimethyluric acid described by Mabery and Hill (Abstr., 1879, 48), is formed by methylating pure lead 3-methylurate, prepared from 3-methylchloroxanthine. As the dimethyluric acid is converted by hydrochloric acid and potassium chlorate into methylcarbamide and methylalloxan, it follows that it is a 3:9-derivative.

3:9-Dimethyluric acid yields a considerable amount of 2:6-dichloro-8-oxy-9-methylpurine when treated with phosphorus oxychloride and pentachloride, the methyl group in position 3 being removed. This explains the fact that a crude methyluric acid, containing both 3- and 9-methyluric acids, as well as 3:9-dimethyluric acid, yields more of the 9-methylpurine derivative than corresponds with the amount of the 9-methyluric acid present.

7-Methyluric acid is converted by phosphorus oxychloride into 2:6-dichloro-8-oxy-7-methylpurine, and this, when treated with phosphorus pentachloride, yields 7-methyltrichloropurine; if, however, the oxy-compound is heated with excess of phosphorus oxychloride at 150—160°, it yields a compound,  $C_{10}H_7N_6OCl_3$ , which crystallises in slender, colourless needles, melts at 281° (corr.), is decomposed by alkalis, and on treatment with hydriodic acid yields 8-oxy-7-methylpurine.  
A. H.

**Solubility of Coniine in Carbon Bisulphide.** By HERM. MELZER (*Arch. Pharm.*, 1898, 236, 701—703).—According to Blyth (*Annalen*, 1849, 70, 77), coniine is but sparingly soluble in carbon bisulphide, but according to the author, this alkaloid readily combines with it, yielding *coniine coniyllthiocarbamate*,  $C_3H_7 \cdot C_5H_9NH \cdot C_3H_7 \cdot C_5H_9N \cdot CS \cdot SH$ . This is best obtained by mixing ethereal solutions of the two constituents in equivalent quantities, evaporating the ether under diminished pressure, and crystallising the residue from light petroleum; it forms colourless needles melting at 71—72°, and is readily soluble in all the ordinary solvents.

When hydrogen sulphide is passed into a dry ethereal solution of coniine, crystalline needles are deposited, but rapidly deliquesce when exposed to the air.  
J. J. S.

**Triacetylmorphine and the Oxidation of Morphine.** By HENRI CAUSSE (*Compt. rend.*, 1899, 128, 181—183).—Ten grams of morphine are dissolved in 150 grams of acetic anhydride, 10 grams of dry and fused sodium acetate, and 10 grams of zinc powder are added, and the mixture is boiled in a reflux apparatus until all the zinc has dissolved. After cooling, the crystalline mass is suspended in acetic anhydride, the liquid drained off, distilled, the residue purified in the usual way, and finally crystallised from methylic alcohol. The *triacetylmorphine*,  $C_{23}H_{27}NO_6 + H_2O$ , obtained in this way loses its water of hydration at 115°; the hydrate melts at 155° and the anhydrous salt at 158°, which is lower than the melting point of either the mono- or di-acetyl derivatives. Triacetylmorphine is soluble in methylic or ethylic alcohol, but insoluble in cold solutions of caustic alkalis or alkali carbonates; it gives no coloration with ferric chloride, selenious anhydride or nitric acid. Its salts are very soluble and crystallise with difficulty, but the oxalate can be obtained in silky crystals. The formation of a triacetyl derivative under the conditions described may be attributed to

reduction of the carbonyl group CO to COH by the hydrogen resulting from the action of the zinc on the acetic acid formed.

When morphine is dissolved in acetic acid and boiled with iodic acid in an atmosphere of oxygen, it loses one molecular proportion of carbonic anhydride for each molecular proportion of morphine.

From these facts, it follows that the third oxygen atom exists in the morphine as a carbonyl group CO, this group and two hydroxyl groups being directly united with the nitrogen.

C. H. B.

**Precipitates in Extr. Fluid. Hydrastis.** By OTTO LINDE (*Arch. Pharm.*, 1898, 236, 698—701. Compare Schmidt and Kerstein, *Abstr.*, 1890, 649).—The precipitates formed after some time in liquid extracts of *Hydrastis* differ in composition. The chief constituents are usually berberine and hydrastine, and sometimes small quantities of phytosterol. The amount of hydrastine is small when its slight solubility in alcohol is considered.

J. J. S.

**Is Hydrastine Free or Combined in Hydrastis Rhizome and in the Liquid Extract?** By OTTO LINDE (*Arch. Pharm.*, 1898, 236, 696—698).—According to Dohme and Engelhardt (*Pharm. Rund.*, 1895, 235), part of the hydrastine in *Hydrastis* rhizome is present in the free form and part in the form of salts. Determinations made by the author indicate that there is no definite numerical relationship between the free and combined hydrastine.

J. J. S.

**Hyoscyamus Muticus.** By JOHANNES GADAMER (*Arch. Pharm.*, 1898, 236, 704. Compare Dunstan and Brown, *Trans.*, 1899, 72).—The chief alkaloid of Egyptian *Hyoscyamus muticus* is hyoscyamine. Scopolamine has not been found, but small quantities of atropine have been isolated.

J. J. S.

**Epinephrine.** By JOHN J. ABEL (*Proc. Amer. Physiol. Soc.*, 1898, 3—4, 4—5. *Amer. J. Physiol.*, 2).—*Epinephrine*, the active material of suprarenal capsules, can be separated from aqueous extracts as a benzoate. It is alkaloidal in nature, and has the formula  $C_{17}H_{15}NO_4$ . Various salts were prepared, but most of these are inactive; the chemical operations involved reduce their activity. If the benzoate is decomposed in an autoclave in the presence of a 1 or 2 per cent. solution of sulphuric acid, at a pressure of from 3 to 5 atmospheres, intensely active solutions are obtained. The picrate prepared from the benzoate by direct precipitation with sodium picrate is also active, although it is contaminated with a picrate of unknown composition, but containing a high percentage of nitrogen. The sulphate is also active. The benzoate loses acetic acid on drying.

W. D. H.

**Cynarasin.** By GIOVANNI EMILIO RASETTI (*L'Orosi*, 1898, 21, 289—302).—An aqueous infusion of the flowers of the wild artichoke (*Cynara cardunculus*, L.) is used instead of rennet in the manufacture of a certain kind of Italian cheese, and the author describes a number of experiments which prove that the coagulating power of the infusion is due to the presence therein of a soluble ferment, since it is not affected by the addition of antiseptics and is due neither to the

natural acidity of the liquid nor to micro-organisms. A temperature of about  $50^{\circ}$  is most favourable to the action of the ferment, whilst coagulation is altogether prevented by heating above  $65^{\circ}$ . The ferment, for which the name *cynarasin* is proposed, is precipitated, on adding alcohol to its solution, as a brown, amorphous powder, soluble in water. The aqueous solution is neutral, does not coagulate on heating, froths strongly on agitation, gives no coloration with tincture of guaiacum, gives a brown precipitate with basic lead acetate, is rendered slightly turbid by acetic acid and potassium ferrocyanide, and rather more turbid by nitric acid, picric acid, and the chlorides of mercury, gold, and platinum. Cynarasin is capable of coagulating 150,000 times its weight of milk, but has no action on starch or albumin; it contains carbon, hydrogen, oxygen, and nitrogen (7.17 per cent.), but neither sulphur nor phosphorus. N. L.

Products of the Digestion of Albumin. II. Isolation of the so-called Carbohydrate Group of Egg-albumin. By SIGMUND FRÄNKEL (*Monatsh.*, 1898, 19, 747—769).—When egg-albumin, carefully freed from globulin and ovomucoid, is heated with aqueous baryta, a compound is produced in small quantity which is a snow-white, non-hygroscopic, indistinctly crystalline powder, becomes brown at  $160^{\circ}$  and decomposes at  $200^{\circ}$  without melting. It is readily soluble in water, sparingly in alcohol, gives a very intense reaction with  $\alpha$ -naphthol and sulphuric acid, and does not reduce Fehling's solution, or give the biuret reaction. It gives no red coloration with phloroglucinol and hydrochloric acid, and does not yield furfuraldehyde when distilled with phosphoric acid. After boiling with dilute acids, it yields a substance capable of reducing Fehling's solution and forming an *osazone* melting at  $204^{\circ}$ . This substance, for which the author proposes the name *albumine*, has the composition  $2(C_6H_9O_4 \cdot NH_2) + H_2O$ , and is dextrorotatory,  $\alpha_D = 30.22^{\circ}$ , with benzoic chloride, it yields a crystalline derivative which melts at  $195^{\circ}$ , and thus resembles glucosamine in many respects, being most probably either identical or isomeric with it. A similar product has been obtained from egg-albumin by digestion with pepsin and hydrochloric acid, and also by digestion with trypsin.

The sugar produced from albumin in cases of diabetes, is probably derived from a much more complete disintegration of the albumin molecule than that represented by the formation of albumine, as the yield of this substance is insufficient to account for the amount of sugar excreted by diabetic patients. A. H.

Melanins. By WALTER JONES (*Proc. Amer. Physiol. Soc.*, 1898, 6; *Amer. J. Physiol.*, 2).—A black pigment, which does not contain sulphur, was obtained from a hydrochloric acid extract of horse hair. By oxidation in an alkaline medium, carbonic anhydride and ammonia are obtained; in an acid medium, intermediate products, namely, a substance resembling putrescin, and a light-yellow pigment,  $C_{18}H_{11}N_5O_{10}$ , are also obtained. W. D. H.

## Organic Chemistry.

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**Explosibility of Acetylene at Low Temperatures.** By GEORGES CLAUDE (*Compt. rend.*, 1899, 128, 303—304).—Under atmospheric pressure and at  $-80^{\circ}$ , acetone dissolves more than 2000 times its volume of acetylene. Explosion does not occur on immersing in the solution a platinum wire heated to redness by an electric current, although Berthelot and Vieille have stated that a similar cause readily brings about an explosion in the case of a solution of the gas prepared at the ordinary temperature under a pressure of 20 atmospheres. Liquid acetylene at  $-80^{\circ}$ , under a pressure of 1.3 atmospheres, is not exploded by a heated wire, so that under these conditions the gas can be liquefied without danger.

W. A. D.

**Action of Sulphuric Acid on Acetylene.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 333—339).—The potassium salt of the acid derived from the action of sulphuric acid on acetylene, previously described (this vol., i, 264), has the composition  $3C_2H_2, 4KHSO_4$ . Ordinary sulphuric acid absorbs only a small quantity of acetylene, but the product yields a minute quantity of phenol when heated with potassium hydroxide at  $250^{\circ}$ . A similar result is obtained when the fuming acid acts on aldehyde or paraldehyde.

Acetylene hydrate is formed in very small quantity when the gas is absorbed by fuming sulphuric acid, but the yield is larger with the ordinary acid and still larger with the acid  $H_2SO_4 + H_2O$ . If the product from the monohydrate is diluted with water and distilled, it yields crotonaldehyde mixed with either ethylenic glycol or "vinyl alcohol." When the distillate is treated with silver oxide and the insoluble products containing excess of silver oxide are treated with hydrogen sulphide, a thio-acid, most probably thioglycolic or thiohydroxyglycolic acid, is formed.

C. H. B.

**Action of Chlorine on Chloroform and Bromine on Bromoform in Presence of the Corresponding Aluminium Halogen Salts.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 179—180).—In the methane series, the aluminium compound has practically no effect in promoting further substitution. In the higher series, this agent first induces the formation of unsaturated compounds with which the halogen forms additive products.

G. T. M.

**Decomposition of Iodoform by Light.** By EDWARD KREMERS and E. C. W. KOSKE (*Pharm. Archives*, 1898, 1, 194—200).—The decomposition of iodoform by light does not reach a limit as Fleury states (*J. Pharm.*, [vi], 6, 97), but is dependent on the amount of iodoform, the length of exposure, and, above all, on the nature of the light—whether direct sunlight or indirect, that is, light which has passed through a solution of iodine in potassium iodide. By exposing an alcoholic solution of iodoform to direct sunlight for 30 minutes 1.9—2.12 per cent. of the iodine contained in the iodoform was

liberated, in 1 hour 2·87—3·23, and in 3 hours 4·86—5·51. Indirect exposure, however, only caused a liberation of 0·386—0·503 per cent. in 30 minutes, 0·353—0·806 in 1 hour, and 0·416—1·14 in 2 hours. When iodine has been liberated and dissolved, the colour of the solution largely protects the rest of the iodoform from decomposition, by absorbing the actinic rays, but Fleury's proof of this is invalid, for when an alcoholic solution of iodoform containing precipitated metallic silver was placed in the dark for 3 days, 80·4 per cent. of the iodine was obtained as silver iodide, after 4 days 81, and after 7 days 98·1 per cent.

E. W. W.

**Chemical Behaviour of Iodoform, and its Detection in Aqueous Solutions.** By LUDWIG VON STUBENRAUCH (*Chem. Centr.*, 1898, ii, 1285; from *Zeit. Unters. Nahr.-Genussm.*, 1898, 737—741).—Iodoform acts on concentrated solutions of silver nitrate, forming carbonic oxide, nitric acid, and silver iodide, and when triturated with silver nitrate, it decomposes with explosive violence, forming dense fumes of iodine, silver iodide, nitrogen oxides, and probably carbonic oxide. When iodoform is suspended in water and exposed to sunlight, free iodine and probably also hydrogen iodide are formed and dissolved. If iodoform suspended in water is warmed with zinc dust and acetic acid, the filtrate gives a blue coloration when starch paste and a drop of fuming nitric acid are added. This reaction is used as a test for iodoform, but is only trustworthy when the solution to be tested does not contain an iodide, hydriodic acid, or an easily decomposed organic substance containing iodine, and hence does not give a blue coloration when fuming nitric acid and starch paste are added without previous reduction. The test is also inapplicable when the solution contains appreciable quantities of albumin.

E. W. W.

**Liquid Acetylene Di-iodide.** By EDWARD H. KEISER (*Amer. Chem. J.*, 1899, 21, 261—265. Compare Sabanéeff, this Journal, 1876, i, 55; and Paternò and Peratoner, *Abstr.*, 1890, 1219).—Acetylene has no action on iodine in the cold, but when dry acetylene is gently warmed with some solid iodine, the gas is slowly absorbed; the reaction is best carried out at 140—160°, and the colour of the iodine usually disappears in the course of 24—36 hours. The product, when cold, consists of a mass of crystals of the ordinary solid di-iodide (m. p. 73°), and an amber-coloured liquid, the yield of the latter being apparently greater if the temperature of the bath is kept at 150—160° than if at 120—130°; when cooled, the liquid gives a further separation of the solid di-iodide, and if cooled at -23° solidifies, but partially melts when the temperature is slowly raised. By this process of solidification and partial fusion, or by fractional solution in 50 per cent. alcohol in which the solid di-iodide is practically insoluble, the liquid can be separated into its two constituents, the solid and a liquid di-iodide.

Liquid acetylene di-iodide is colourless, but in diffused daylight slowly turns violet; it boils at 185°, solidifies at -21°, has a sp. gr. of 3·0625 at 20°, is readily volatile with steam, and is insoluble in water but readily soluble in alcohol and organic solvents. The



vapour can be heated to  $230^{\circ}$  without undergoing decomposition. When left in contact with hydriodic acid, it is slowly transformed into the solid modification, and when treated with zinc dust and alcohol it yields acetylene. The two di-iodides are supposed to be stereoisomerides, the solid being regarded as the *trans*- and the liquid as the *cis*-modification.

J. J. S.

**Direct Nitration of Paraffins. Higher Primary Nitro-paraffins.** By R. A. WORSTALL (*Amer. Chem. J.*, 1899, 21, 210—218 and 218—238. Compare *Abstr.*, 1898, i, 346).—Nonane, decane, hendecane, and dodecane have been nitrated according to the method previously described, and, in addition to nitro-derivatives, acetic, oxalic, and succinic acids and carbonic anhydride were always formed. With nonane, nitric acid of sp. gr. 1.08 was employed, and a 70 per cent. yield of mono- and dinitro-derivatives was obtained. Acid of the same strength was employed for decane, hendecane, and dodecane; the nitro-derivatives were separated from unaltered hydrocarbon by conversion into sodium derivatives, which were extracted by water, decomposed by carbonic anhydride, and the nitro-derivatives extracted with ether, the mononitro- being separated from the dinitro-compounds by distillation in steam.

Nitrohexane boils at  $180$ — $181^{\circ}$ , has a sp. gr. of 0.9605 at  $17^{\circ}$ , and yields hexoic acid when heated with concentrated hydrochloric acid at  $160^{\circ}$ . It is only slowly soluble in aqueous potassium hydroxide, but readily in alcoholic potash. The best method for obtaining its sodium derivative,  $C_6H_{12}Na \cdot NO_2$ , is to add a solution of sodium ethoxide in a mixture of alcohol and light petroleum to a solution of the nitro-compound in light petroleum; it is a colourless salt readily soluble in water or alcohol, but insoluble in ether or carbon bisulphide; it blackens when heated, but is not explosive. Dinitrohexane reacts with bromine water, yielding a heavy, oily bromide; when reduced, the dinitro-compound yields ammonia as one product.

Nitroheptane boils at  $193$ — $195^{\circ}$ , and has a sp. gr. of 0.9476 at  $17^{\circ}$ ; its sodium, mercuric, lead, and silver salts have been prepared. When the sodium derivative is added to an excess of bromine water, a heavy, oily bromide,  $C_7H_{14}BrNO_2$ , is obtained.

Nitro-octane boils at  $206$ — $210^{\circ}$ , and has a sp. gr. of 0.9346 at  $20^{\circ}$ . Dinitro-octane has a sp. gr. of 1.0638 at  $23^{\circ}$ .

*Nitrononane*,  $C_9H_{19}NO_2$ , is a pale yellow liquid with a pleasant odour; it boils at  $215$ — $218^{\circ}$ , but undergoes considerable decomposition, and has a sp. gr. of 0.9227 at  $17^{\circ}$ . Dinitrononane has not been obtained in a pure state.

The sp. gr. of *nitrododecane* at  $15^{\circ}$  is 0.9105, that of *nitrohendecane* is 0.9001; the amount of nitrododecane obtained was too small to admit of purification.

The sodium derivatives, nitrolic acids, and bromo-derivatives of most of these nitro-compounds are described; the amines and corresponding platinochlorides were also prepared.

J. J. S.

**Determination of the Structure of Substances with Labile Atom-groupings.** By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 575—600).—The author describes as *pseudo-acids* those substances which do not

contain a hydrogen atom directly displaceable by metals, but which are capable of changing into a salt-forming isomeride. The following tests may be used to recognise the existence of pseudo-acids. (1) If an aqueous solution of a hydrogen compound neutralises a base *gradually*, it is a pseudo-acid. (2) If a neutral or feebly acid hydrogen compound gives salts which are neutral or feebly basic, that is, are not dissociated hydrolytically, it is a pseudo-acid, and the salts are derived from a more strongly acid isomeride. In a case of this sort, a neutral solution of the salt, when mixed with an equivalent quantity of an acid, still remains neutral. (3) If a colourless hydrogen compound yields coloured salts and a coloured ion in solution, it is a pseudo-acid. (4) An abnormally large positive temperature coefficient in the conductivity or the dissociation constant of a solution, is an indication of a pseudo-acid. (5) If a hydrogen compound does not form a salt by direct combination with dry ammonia in a non-dissociating solvent, but does so in presence of water, it is a pseudo-acid; the formation of a salt, however, does not prove it to be a true acid. Similarly, if phenylcarbimide, phosphorus pentachloride, and acetic chloride do not interact with a substance except in dissociating solvents, it is probably non-hydroxylic pseudo-acid. (6) If a substance does not combine directly with water or alcohol, but yields a stable hydrate or alcoholate by indirect methods, it is a pseudo-acid.

Most of the examples quoted in the paper are referred to in the succeeding abstracts, but the following are new. Violuric acid and other oximidoketones,  $-\text{CO}\cdot\text{C}(\text{NOH})-$ , are colourless, but yield coloured salts derived probably from the form  $-\text{C}(\text{OH})\text{:C}(\text{NO})-$ ; paranitrophenol behaves similarly; in all these cases, there is a very great increment in the conductivity of a solution between  $0^\circ$  and  $25^\circ$ , which is accompanied by a deepening in the colour of the solution. The antidiazohydrates,  $\text{R}_1\cdot\text{N}\text{:NOH}$ , which are electrolytes, and therefore true acids, interact with phosphorus pentachloride, acetic chloride, and ammonia, but the non-electrolytic nitrosamines,  $\text{R}_2\cdot\text{NH}\cdot\text{NO}$ , do not; Thiele's 'nitrosourethane' belongs to the former class, and is formulated by the author as  $\text{COOEt}\cdot\text{N}\text{:N}\cdot\text{OH}$ , whilst 'parabromodiazobenzene' is formulated as  $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NO}$ . The potassium derivative of hydroxyazobenzene,  $\text{C}_6\text{H}_5\cdot\text{N}\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{OK}$ , by interaction with hydrochloric acid in aqueous solution, yields a hydrate which cannot be prepared directly by the action of water on the parent substance; the latter is therefore regarded as the isomeric quinone hydrazone,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}\text{:C}_6\text{H}_4\text{:O}$ .

When the salt-forming modification of a substance is not known in a free state, but only in the salts, or as an ion in aqueous solution, the author describes the case as one of '*ionisation isomerism*.'

*Pseudo-bases* are substances which, by isomeric change, are capable of giving a true base of the ammonium hydroxide type from which the salts are derived. Thus phenylmethyiacridinium chloride,

$\text{CPh} \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{NMeCl}$ , is converted by alkalis into phenylmethyl-

acridinium hydroxide,  $\text{CPh} \begin{array}{c} \swarrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{NMe}\cdot\text{OH}$ , which is almost as power-

ful a base as potash, and is highly dissociated in solution, but rapidly changes into the isomeric phenylmethylnitrosol,  $\text{CPh(OH)}\langle\text{C}_6\text{H}_4\rangle\text{NMe}$ , which is an indifferent alcoholic pseudo-base, insoluble in water, and readily soluble in organic solvents. A large number of other ammonium-bases are referred to in the paper as probably belonging to the same class.

T. M. L.

NOTE.—It has been shown by Brereton Baker (Proc., 1893, 9, 129, 165) that ammonia and hydrogen chloride do not combine except in presence of moisture; hydrogen chloride would therefore be classified as a 'pseudo-acid,' according to the rules given in this paper. The chemical tests under the fifth heading do not, therefore, appear to be altogether trustworthy. The majority of the tests are only applicable to those cases in which the conversion of the free acid into the neutral pseudo-acid is virtually complete.

T. M. L.

**Isonitro-compounds.** By ARTHUR HANTZSCH and A. VEIT (*Ber.*, 1899, 32, 607—627. Compare Abstr., 1896, i, 353 and 672).—Nitromethane is a normal nitro-compound; it has no acid reaction, yields solutions of very low conductivity, and gives no coloration with ferric chloride. The salts, which are derived from isonitromethane, show an alkaline reaction, and give a red coloration with ferric chloride. The existence of isonitromethane in a free state is shown by the following facts. (1) When a cold solution of the sodium salt is acidified with hydrochloric acid, it gives a transient red coloration with ferric chloride. (2) A mixture of equivalent quantities of nitromethane and baryta water shows a decrease of conductivity during 15 minutes at  $0^\circ$ , as the base is *gradually* neutralised by the pseudo-acid. (3) Similarly, when a solution of the barium salt is mixed with an equivalent quantity of hydrochloric acid, the conductivity falls, during about 15 minutes, to that of the barium chloride in the solution, as the isonitromethane first formed passes into normal nitromethane. (4) When the barium salt is titrated with an equivalent quantity of hydrochloric acid, using methyl-orange as an indicator, a red colour appears on each addition of acid, but disappears again as the acid isonitromethane is converted into neutral nitromethane; a permanent red is first obtained when one equivalent of acid has been added to the salt, and the solution then ceases to give a red colour with ferric chloride. An aqueous solution of barium isonitromethane gradually decomposes into nitrous acid, hydroxylamine, formaldehyde, or formoxime, formic acid, and hydrocyanic acid. On adding acid to a concentrated solution of sodium isonitromethane, an intense red colour appears at the moment of neutralisation, but disappears with an excess of acid; this indicates the formation of methylnitrosol,  $\text{NO}_2\cdot\text{CH}\cdot\text{NOH}$ .

Bromonitromethane does not give any coloration with ferric chloride, and is a non-electrolyte. The sodium salt gives an intense coloration with ferric chloride, which persists for some time when the solution is acidified; the bromisonitromethane, the presence of which is thus indicated, changes into the normal form at least as rapidly as isonitro-

methane, but soon decomposes into hydrogen bromide, nitrous acid, and other products.

Dibromonitromethane behaves similarly, but the salts are still more unstable.

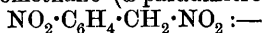
**Nitroethane:**—Sodium isonitroethane gives a deep blood red coloration with ferric chloride, which persists for half an hour in the acidified solution; isonitroethane could not, however, be isolated. On passing hydrogen chloride into the sodium salt suspended in ether, a transient blue coloration appears, and ethylnitric acid is produced. The barium salt is alkaline, and behaves like barium isonitromethane when titrated with hydrochloric acid; if the whole of the acid is added at once, about 5 per cent. of the isonitroethane is decomposed into hyponitrous acid and aldehyde; this decomposition only takes place with excess of acid, thus explaining the contradictory statements of Nef (Abstr., 1895, i, 3) and V. Meyer (Abstr., 1895, i, 197). The neutralisation of nitroethane by caustic soda occupies about 40 minutes at 0°, but only 3 minutes at 25°, as indicated by the conductivity. The fall of conductivity on neutralising the barium salt with hydrochloric acid occupies about 2 days at 25°. Isonitroethane is about as strong an acid as acetic.

Nitropentane, contrary to the statement of V. Meyer (this Journal, 1872, 474), forms a sodium salt; this has an alkaline reaction, and with ferric chloride gives a red coloration, which also appears in a freshly acidified solution.

**Phenylnitromethane ( $\omega$ -nitrotoluene):**—The ammonium salt, which melts at 89–90°, is precipitated by dry ammonia from a solution of the iso-, but not of the normal, nitro-compound; phenylisonitromethane also interacts with phenylcarbimide and with phosphorus pentachloride, but no definite product was isolated. On titrating the sodium salt with hydrochloric acid, the solution only becomes neutral very slowly, owing to the great stability of isophenylnitromethane; about 5 per cent. of the substance is decomposed into benzaldehyde and nitrous oxide.

**Bromophenylnitromethane ( $\omega\omega$ -bromonitrotoluene),  $CPhBr \cdot NO_2$ ,** is indifferent to ferric chloride, but the sodium salt yields an intense black colour with ferric chloride; the sodium salt decomposes in the solid state and very rapidly in solution, with formation of sodium bromide; the free isonitro-compound is still more unstable.

**Paranitrophylnitromethane ( $\omega$ -paradininitrotoluene),**



The isonitro-compound described by Holleman (Abstr., 1897, i, 409) can be kept in a desiccator for a day before it loses its ferric chloride reaction, but it is much less stable in solution, the order of decreasing stability being given by the series,—chloroform, benzene, ether, alcohol, water. The isonitro-compound, unlike the normal form, interacts with phenylcarbimide and with phosphorus pentachloride. The sodium, ammonium, and copper salts each exist in two modifications. Paranitrophylnitromethane is very sensitive to the action of excess of alkali, which decomposes it into sodium nitrite and a substance melting at 225°, which is probably a stilbene derivative.

Isonitracetophenone yields a neutral sodium salt, for which

$\lambda_{\infty} = 74.0$ ; from this,  $\lambda_{\infty}$  is calculated to be 24.8 for the anion, and 350 for the acid. The dissociation-constant of isonitracetophenone is  $K = 0.0063$ , and it is therefore a stronger acid than benzoic. Since the acid modification is stable in solution, the conductivity immediately reaches a constant value on mixing equivalent quantities of the sodium salt and hydrochloric acid, or of the isonitro-compound and caustic soda.

Isonitracetone [see footnote, this vol., i, 433] yields a neutral sodium salt which does not colour a solution of potassium iodide and starch; isonitracetone itself decomposes rapidly even at  $0^{\circ}$ , and although a very good electrolyte, it does not show a constant conductivity.

Potassium isodinitromethane is neutral and gives no coloration with ferric chloride; from the conductivity of an aqueous solution, the molecular conductivity of isodinitromethane was calculated to be  $\lambda_{\infty} = 237$  at  $0^{\circ}$ . The dissociation constant, determined from a mixture of the potassium salt with hydrochloric acid, was  $K = 0.0143$ , whilst a mixture of the silver salt with hydrochloric acid gave  $K = 0.0138$  at  $0^{\circ}$ ; at  $25^{\circ}$ ,  $\lambda_{\infty} = 369$  and  $K = 0.0268$ ; isodinitromethane is therefore about 8 times as strong as acetic acid. The large temperature coefficient for  $K$  shows that the aqueous solution contains normal as well as iso-dinitromethane; the colourless oil which is obtained by extracting with ether has an acid reaction and is probably also a mixture (compare nitracetone).

Bromodinitromethane.—A mixture of the potassium salt with hydrochloric acid was found to have a constant conductivity, showing that the isonitro-compound does not pass over into the normal form in aqueous solution; subtracting the value for potassium chloride,  $\lambda = 20.1$  for a concentration  $N/64$ ; this substance is a stronger acid than dinitromethane.

Dinitroethane behaves quite differently from dinitromethane, and resembles rather mononitromethane. The conductivity of a mixture of the potassium salt with an equivalent quantity of hydrochloric acid falls after about a quarter of an hour at  $0^{\circ}$  to that of the potassium chloride in the solution, owing to the conversion of the isodinitroethane into the normal form. On titrating a solution of the potassium salt with an equivalent quantity of hydrochloric acid, results are obtained similar to those which have been described for barium isonitromethane; the isonitro-compound is, however, more labile, and the red coloration never lasts more than 30 seconds. The resulting solution still contains a trace of isodinitroethane (although this cannot be determined from the conductivity), since it is acid to litmus and is still slightly yellow; the yellow colour only disappears when an excess of acid has been added.

The authors point out that amongst the derivatives of nitromethane the stability of the isonitro-compound and its acid character increases with the negative character of the radicle, as is seen in the series isonitro-methane and -ethane, phenyl-isonitromethane, parabromo- and paranitro-phenylisonitromethane, benzoyl- and acetyl-isonitromethane (isonitracetophenone and isonitracetone).

T. M. L.

**Nitroform.** By ARTHUR HANTZSCH and A. RINCKENBERGER (*Ber.*, 1899, 32, 628—641).—By the action of alcoholic potash, tetranitromethane is converted into ethylic nitrate and *potassium nitroform*. This is a yellow salt, which explodes between 97° and 99°, and gradually decomposes at ordinary temperatures, leaving a residue of pure potassium nitrate, according to the equation  $2C(NO_2)_3K = 2KNO_3 + 2CO_2 + 2NO + N_2$ . The aqueous solution is yellow, the molecular conductivity is  $\lambda_{32} = 51.9$  at 0°, and at 25°  $\lambda_{32} = 98.3$ ,  $\lambda_{1024} = 111.2$ , the difference  $\lambda_{1024} - \lambda_{32}$  being exactly the same as for potassium chloride. The *sodium* salt gave  $\lambda_{32} = 80.2$ ,  $\lambda_{64} = 83.0$ , whence  $\lambda_\infty = 94.1$ , and for the acid  $\lambda_\infty = 325 + 45 = 370$  at 25°. The *ammonium* salt explodes at 200°, and decomposes slowly at ordinary temperatures, leaving a residue of ammonium nitrate.

On adding an excess of sulphuric acid to a solution of potassium nitroform, the yellow colour disappears, and, by extracting with ether, normal nitroform can be obtained in colourless crystals melting at 15°. Anhydrous solutions of nitroform in benzene, light petroleum, chloroform, carbon bisulphide, and absolute ether are colourless, but the merest trace of water develops the yellow colour characteristic of isonitroform. Whilst isonitromethane is a very feeble acid, isodinotromethane is a fairly strong acid, and isonitroform is one of the strongest organic acids, the degree of dissociation being too high to determine the affinity constant; thus, at 25°, the degree of dissociation is 88.1 per cent. at  $N/32$ , and 94.9 per cent. at  $N/512$ , whilst at 0° it is 96.7 per cent. at  $N/512$ . The temperature coefficient of conductivity is comparable with that of hydrochloric acid. The strength of the acid is illustrated by the fact that the degree of dissociation is not altered by mixing with an equivalent quantity of hydrochloric acid; the solution has a mean conductivity, and it is only when there is a very large excess of the mineral acid that the yellow colour of the ion begins to disappear. Contrary to the statement of V. Meyer (this Journal, 1875, 1256), nitroform is quite a stable substance, and can be distilled with steam either alone or in presence of sulphuric acid; the vapour is colourless, and the substance, therefore, distils as true nitroform, but condenses to a yellow solution.

The *silver* salt,  $C(NO_2)_3Ag + H_2O$ , dissolves in water or ether, and is regarded by the author as having the formula  $CH(NO_2)_2 \cdot NO(OH) \cdot OAg$ , corresponding with that of the alcoholates described later; it is neutral, melts at 100°, decomposing at 106°, and slowly at ordinary temperatures. By interaction with methylic iodide, it yields trinitroethane  $CMe(NO_2)_3$ , identical with that described by Franchimont (*Abstr.*, 1887, 466). In just the same manner as tetranitromethane is converted into trinitromethane and ethylic nitrate by the action of alcoholic potash, trinitromethane is converted by the action of aqueous potash into potassium dinitroethane and potassium nitrate; the product is identical with the potassium salt prepared by Chancel (*Abstr.*, 1883, 914) and by ter Meer (*Abstr.*, 1876, ii, 185) from the product of the action of nitric acid on ethylic methylacetoacetate. If alcoholic potash is used, the product is an *alcoholate*, to which the author ascribes the formula  $CHMe(NO_2) \cdot NO(OK) \cdot OEt$ ; this

salt is very stable, it separates from alcohol in yellow leaflets and also crystallises unaltered from hot water in long, slender needles; it differs entirely from the potassium salt of dinitroethane, and gives a silver salt which also contains 1 mol. of alcohol. The corresponding acid, *dinitroethane alcoholate*, was obtained as a yellow oil with a faint smell and slight acid reaction; unlike dinitroethane, this acid, when prepared from the potassium salt and hydrochloric acid, does not pass into an indifferent pseudo-acid, but remains as a true acid for which  $\lambda\infty = 356.4$  and  $K = 0.0164$  at  $25^\circ$ ; it is thus ten times as strong as acetic acid. The alcohol was not removed from the potassium salt by boiling with water or by dissolving in sulphuric acid, and, conversely, the alcoholates could not be prepared by the action of alcohol on dinitroethane or its potassium salt; the series of compounds is similar to the compounds of sodium methoxide with trinitrobenzene (V. Meyer, Abstr., 1896, i, 419), and with picric ethers (Jackson and Ittner, Abstr., 1897, i, 332; and Jackson and Boos, Abstr., 1898, i, 517).

T. M. L.

**Cyanoform.** By ARTHUR HANTZSCH and G. OSSWALD (*Ber.*, 1899, 32, 641—650. Compare Schmidtman, Abstr., 1896, i, 458).—When cyanoform is shaken up with water and ether, three layers are produced (Schmidtman) just as is the case with water, ether, and succinonitrile (Schreinemaker, Abstr., 1898, ii, 329); the composition of the middle layer is fairly constant, and may be represented roughly by the formula  $\text{CH}(\text{CN})_3 + 10\text{H}_2\text{O} + 10\text{Et}_2\text{O}$ .

Pure cyanoform rapidly polymerises to a yellow, crystalline mass (Schmidtman), as is readily seen on allowing an ethereal solution to evaporate, but the aqueous solution is remarkably stable, although it acquires a greenish-yellow colour by exposure to air; it can be titrated sharply with caustic soda and phenolphthalein, and is unaltered by boiling with dilute acids and alkalis; it is not appreciably volatile with steam. The aqueous solution appears to consist chiefly of *isocyanoform*,  $\text{C}(\text{CN})_2 \cdot \text{C} \cdot \text{NH}$ , and it is from this that the salts are derived.

*Sodium isocyanoform* has a molecular conductivity  $\lambda\infty = 91.4$ , from which the molecular conductivity of the acid is calculated to be  $\lambda\infty = 367$ . Isocyanoform is an even stronger acid than isonitroform, the degree of dissociation being 92.5 per cent. at N/32, and 97.6 per cent. at N/1024 at  $25^\circ$ . *Ammonium cyanoform*,  $\text{C}(\text{CN})_2 \cdot \text{C} \cdot \text{N} \cdot \text{NH}_4$ , is a well-crystallised neutral salt, and melts with decomposition at  $183^\circ$ ; with excess of ammonia, it gives a liquid product which has approximately the composition  $\text{CH}(\text{CN})_3 \cdot 3\text{NH}_3$ ; this is analogous to the liquid product formed by ammonium nitrate (Divers, Abstr., 1873, 598; 1898, ii, 508).

The alcoholate described by Schmidtman is regarded as dicyanacetimidoethylic ether,  $\text{CH}(\text{CN})_2 \cdot \text{C}(\text{OEt}) \cdot \text{NH}$ ; unlike cyanoform, its aqueous solution is neutral, but slowly becomes acid when boiled as the cyanoform is regenerated; it is insoluble in ammonia, but dissolves in cold caustic soda, from which it is at first precipitated unchanged by acids, but afterwards passes back into cyanoform.

When silver cyanoform is heated with methylic iodide, it is converted into *tricyanoethane*,  $\text{CMe}(\text{CN})_3$ , which sublimes in fine, colourless needles

and melts at  $93.5^\circ$ ; it is readily soluble in all organic solvents except light petroleum, but, unlike cyanoforn, is soluble in water. When boiled with water, it is decomposed into cyanic acid,  $(\text{CO}_2 + \text{NH}_3)$ , and a substance melting at  $60-65^\circ$ , which is probably methylmalonodinitrile,  $\text{CHMe}(\text{CN})_2$ ; when boiled with soda, it is hydrolysed to ammonia and methylmalonic acid.

With benzylic iodide, silver cyanoforn interacts in the cold, forming *tricyanoethylbenzene*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CN})_3$ ; this crystallises from chloroform in yellowish needles, melts at  $138^\circ$ , and sublimes when heated carefully. It is more stable to hot water than tricyanoethane, but readily loses 1 mol. of cyanic acid in alcoholic solution, and is converted into *benzylmalonodinitrile*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CN})_2$ , which is deposited in colourless plates melting at  $78-79^\circ$ ; it is neutral, dissolves in alcohol and ether, but not in water; when boiled with caustic soda, it is decomposed into ammonia and benzylmalonic acid. T. M. L.

**Cyanuric Compounds.** By OTTO DIELS (*Ber.*, 1899, 32, 691—702).—The resemblance between cyanuric derivatives and purine compounds suggested the possibility of reducing cyanuric chloride to the corresponding hydrogen compound,  $\text{C}_3\text{N}_3\text{H}_3$ . Although this step has not been found practicable, chlorocyanurodiamine yields diamidocyanuric hydride under the influence of hydriodic acid; this treatment converts several chlorocyanuramines into the corresponding derivatives of cyanuric hydride.

The symmetrical structure of the cyanuric molecule, represented by the formula  $\text{N} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} \text{N} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} \text{N}$ , is established by replacing single halogen

atoms in cyanuric chloride by three different amido-groups; if this operation is carried out in the three orders possible, the final product is found to be the same in each case.

*Diamidocyanuric hydride*,  $\text{C}_3\text{N}_3\text{H}(\text{NH}_2)_2$ , obtained by agitating chlorocyanurodiamide with fuming hydriodic acid and phosphonium iodide, crystallises from boiling water in long, lustrous needles; it softens at  $320^\circ$ , and melts and decomposes at  $325^\circ$  ( $329^\circ$  corr.). The *hydrochloride*, *nitrate*, and *sulphate* are crystalline, and salts are also formed with the chlorides of platinum, gold, and mercury. The *diacetyl* derivative is insoluble in cold water, and dissolves sparingly in boiling water or acetone.

*Cyanuramidodichloride*,  $\text{C}_3\text{N}_3\text{Cl}_2\cdot\text{NH}_2$ , prepared by passing ammonia into an ice cold ethereal solution of cyanuric chloride, and evaporating in a vacuum the filtrate from the ammonium chloride, crystallises from water, and does not melt below  $400^\circ$ ; it dissolves very readily in alcohol, ether, chloroform, and acetone, and is scarcely soluble in cold water. When treated with boiling water in a reflux apparatus during  $1\frac{1}{2}$  hours, it is converted into melanurenic acid,  $\text{NH}_2\cdot\text{C}_3\text{N}_3(\text{OH})_2$ ; it is also soluble in alkali sulphides, yielding dithiomelanurenic acid,  $\text{NH}_2\cdot\text{C}_3\text{N}_3(\text{SH})_2$ .

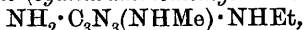
*Amidocyanuric dihydride*,  $\text{C}_3\text{N}_3\text{H}_2\cdot\text{NH}_2$ , produced on agitating cyanuramidodichloride with hydriodic acid and phosphonium iodide, crystallises from hot water in long, silky needles; it softens and



becomes brown at  $215^{\circ}$ , and melts and decomposes at  $225^{\circ}$  ( $228^{\circ}$  corr.). The *aurichloride* forms long, yellow needles.

*Cyanuramidomethylamidochloride*,  $\text{NH}_2 \cdot \text{C}_3\text{N}_3\text{Cl} \cdot \text{NHMe}$ , prepared from cyanuramidodichloride and methylamine, crystallises from acetone in small plates containing  $\frac{1}{2}\text{H}_2\text{O}$ .

*Methylethylmelamine* (*cyanuramidomethylamidoethylamide*),



is obtained by heating the foregoing substance with aqueous ethylamine at  $100$ – $110^{\circ}$  during 3–4 hours; it dissolves readily in hot water, separating slowly from the cold solutions in ill-defined crystals melting at  $174^{\circ}$  ( $176^{\circ}$  corr.). The *hydrochloride*, *sulphate*, and *nitrate* crystallise in needles, the last-named melting at  $166^{\circ}$  (corr.); the *oxalate* melts at  $230^{\circ}$  (corr.), and crystalline salts are also formed with the chlorides of platinum, gold, and mercury.

*Cyanuroethylamidodichloride*,  $\text{C}_3\text{N}_3\text{Cl}_2 \cdot \text{NHEt}$ , prepared by carefully adding an ethereal solution of ethylamine to cyanuric chloride dissolved in ether at  $-20^{\circ}$ , crystallises in silky needles, and melts at  $107.5^{\circ}$  (corr.).

*Cyanuramidooethylamidochloride*,  $\text{NH}_2 \cdot \text{C}_3\text{N}_3\text{Cl} \cdot \text{NHEt}$ , obtained by the action of aqueous ammonia on the foregoing substance, crystallises from hot glacial acetic acid in aggregates of lustrous needles; it sinters at  $170^{\circ}$ , and melts at  $177^{\circ}$  (corr.). When heated with aqueous methylamine at  $120$ – $125^{\circ}$  during 3–4 hours, it yields methylethylmelamine.

*Cyanuromethylamidodichloride*, prepared from ethereal cyanuric chloride and methylamine at  $-20^{\circ}$ , dissolves readily in ether, alcohol, acetone, and chloroform; it crystallises from water in long, silky needles, sinters at  $156^{\circ}$ , and melts at  $163^{\circ}$  (corr.).

*Cyanuromethylamidoethylamidochloride*,  $\text{NHMe} \cdot \text{C}_3\text{N}_3\text{Cl} \cdot \text{NHEt}$ , produced on treating the foregoing substance with aqueous ethylamine, crystallises from glacial acetic acid in stellar aggregates; it sinters at  $225^{\circ}$ , and melts at  $238^{\circ}$  (corr.). Aqueous ammonia at  $110^{\circ}$  converts it into methylethylmelamine.

M. O. F.

**An Isomeride of Potassium Ferricyanide.** By JAMES LOCKE and GASTON H. EDWARDS (*Amer. Chem. J.*, 1899, 21, 193–206). According to Stadeler (*Annalen*, 1869, 151, 1), Bong (this Journal, 1876, i, 907) and Skraup (*ibid.*, 1877, ii, 598), potassium ferricyanide when oxidised, forms the compound  $\text{K}_2\text{FeC}_6\text{N}_6$ . The authors have attempted to prepare it by Skraup's method, but cooled down the liquid so that practically no evolution of gas (cyanogen chloride) occurred; the crystalline product thrown down on the addition of alcohol was purified by dissolving in water and reprecipitating with alcohol. The salt obtained after precipitating thrice with alcohol appeared to be homogeneous under the microscope, and consisted of very small, greenish-yellow needles; after exposure for several days in a vacuum over sulphuric acid, its composition corresponds with that required by the formula  $\text{K}_3\text{FeC}_6\text{N}_6 \cdot \text{H}_2\text{O}$ . This potassium  $\beta$ -ferricyanide, under suitable conditions, may be obtained in olive-coloured crystals of moderate size, and is not hygroscopic; it dissolves with the greatest readiness in water, the solution being comparatively stable,

although it undergoes gradual decomposition. When reduced with sodium amalgam in alkaline solution, it yields potassium ferrocyanide. Like the normal salt, potassium  $\beta$ -ferricyanide yields characteristic precipitates with solutions of salts of most of the heavy metals; these in general have the same characteristics as the  $\alpha$ -ferricyanides, and in some cases pass over into the latter with extreme ease. The bismuth, stannic, lead, and silver salts differ materially from the corresponding  $\alpha$ -ferricyanides. Bismuth  $\alpha$ -ferricyanide is a sparingly soluble, straw-coloured precipitate insoluble in concentrated nitric acid; a solution of potassium  $\beta$ -ferricyanide, when freshly prepared, gives no trace of a precipitate with bismuth nitrate, but after some time, and especially on exposure to bright sunlight, large granules of a black, crystalline compound, probably bismuth ferrocyanide, are deposited. Stannic chloride forms a precipitate with the  $\beta$ -, but not with the  $\alpha$ -isomeric. Lead  $\beta$ -ferricyanide is more readily soluble than the  $\alpha$ -compound, Silver  $\beta$ -ferricyanide is obtained as a dark-brown, flocculent precipitate which can be readily filtered and washed; when suspended in water and heated at  $100^{\circ}$ , it is transformed into the  $\alpha$ -compound.  $\beta$ -Ferri-cyanic acid has not been isolated.

J. J. S.

**Action of Aluminium Amalgam on Alcohols.** By WETSCHIAS-LAW E. TISTSCHENKO (*Chem. Centr.*, 1898, i, 91; from *J. russ. chem. Ges.*, 29).—By the action of aluminium amalgam on alcohols, the corresponding aluminium alkoxides (*J. russ. chem. Ges.*, 28, 412) are obtained. *Aluminium butoxide* boils at about  $285^{\circ}$  under 10–12 mm. pressure, the *iso-amyloxide* at  $281^{\circ}$  under 3.5–4 mm. pressure, and the *isopropoxide* at about  $170^{\circ}$  under 16 mm., and at about  $150^{\circ}$  under 4 mm. pressure. The *aluminium* derivatives of *secondary butylic alcohol* and of *methylpropylcarbinol* were also prepared. Trimethylcarbinol and dimethylethylcarbinol are attacked by the amalgam, but the products were not obtained in a pure state; tertiary amyl alcohol and isobutylic alcohol, however, yield substances which appear to crystallise in colourless needles (compare Hillyer, *Abstr.*, 1897, i, 546). Aluminium amalgam acts on ethylic malonate and ethylic acetoacetate, giving, in the latter case, a compound whose properties are identical with those of Conrad's compound. The action of the amalgam on alcohols is not as violent as that of sodium amalgam; the primary are more easily attacked than the secondary alcohols, with the exception of dimethylethylcarbinol. The lower the molecular weight of the alcohol, the more readily the action takes place, the higher alcoholic groups being easily replaced by the lower, thus the isobutyl-oxide yields the methoxide or ethoxide by the action of methylic or ethylic alcohol, and the aluminium compounds of allylic alcohol, glycol, and ethylic acetoacetate may also be prepared in this way.

E. W. W.

**Decomposition of Barium Isobutylic Sulphate.** By EUG. BIRON (*Chem. Centr.*, 1898, i, 885; from *J. russ. chem. Ges.*, 29, 697–698).—Barium isobutylic sulphate, prepared by Wurtz's method, begins to decompose at  $130^{\circ}$ . The gaseous products were absorbed in hydriodic acid and found to contain two-thirds isobutylene and one-third pseudobutylene.

E. W. W.

**Characteristic Derivatives of Geraniol and Citronellol.** By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 83—88. Compare Abstr., 1898, i, 618).—Geranyl phthalate (*loc. cit.*) yields a crystalline *silver* salt which melts at 132—133° and is very sparingly soluble in boiling water, whilst the *silver* salt prepared from citronellyl phthalate melts at 117—118°. When bromine is added to a solution of geraniol in acetic acid, it gives rise to *geraniol tetrabromide*, a yellow oil which has a sp. gr. 1.424, and cannot be caused to solidify; the corresponding *phthalate*, prepared by adding the calculated quantity of bromine dissolved in five times its weight of glacial acetic acid to a solution of geranyl phthalate in the same solvent, is a non-crystallisable oil which yields a *barium* salt,  $(C_{15}H_{17}O_4Br_4)_2Ba + 4H_2O$ . This is a white powder which is almost insoluble in water, and, when heated, softens at 90°, melts at 95°, and at 125° loses water and decomposes. The *aluminium* salt,  $C_{54}H_{69}O_{17}Br_6Al$ , prepared from the dibromide of citronellyl phthalate, is almost insoluble in water, and decomposes when heated.

The additive compounds, formed by the action of hydrogen bromide on geranyl and citronellyl phthalates, are being studied.

W. A. D.

**Chlorinated Derivatives of Trioxymethylene.** By GIUSEPPE GRASSI-CRISTALDI and C. MASELLI (*Gazzetta*, 1898, 28, ii, 477—500).—The interaction of acetic acid and paraformaldehyde gives a hydrated *trioxymethylene acetate*,  $2CH_2(O\cdot CH_2\cdot OH)_2, 11CH_3\cdot COOH$ , a white, gelatinous mass, gradually melting on heating and boiling at 103.5—104°; on treating it with a large quantity of water, the acetic acid is removed, yielding *trioxymethylene hydrate*,  $CH_2(O\cdot CH_2\cdot OH)_2$ , melting at 107—109°. Cryoscopic determinations show that, in acetic acid solution, trioxymethylene hydrate suffers dissociation with the formation of dioxymethylene (diformaldehyde), which, however, has not been isolated. When dry hydrogen chloride is passed over paraformaldehyde at 130°, symmetrical dichloromethylic ether distils off as a colourless, oily liquid which boils at 104—106°, and undergoes decomposition in contact with moist air; its sp. gr. is 1.322 at 22°, Butlerow's value being 1.315 at 20°. If the paraformaldehyde is heated to 180° and the hydrogen chloride stream increased, methylene chlorhydrin is obtained, in addition to the dichlor-ether already mentioned; the chlorhydrin is a liquid boiling at 166°, and by the action of dehydrating agents is converted into symmetrical dichloromethylic ether. Trioxymethylene acetate absorbs dry hydrogen chloride, forming dichlorotrioxymethylene, or symmetrical dichloromethylal, which boils at 102—104°, and has sp. gr. 1.264 at 22°; cryoscopic measurements show that, in acetic acid solution, it has the normal molecular weight.

When heated with fused sodium acetate, dichlorotrioxymethylene gives the diacetyl derivative of dihydroxymethylic ether,  $O(CH_2\cdot OAc)_2$ , which boils at 208—209°, is insoluble in water, but dissolves in alcohol, ether, acetic acid, and benzene, and in the last-named solvent gives the normal depression of freezing point. The corresponding trioxymethylene acetate,  $CH_2(O\cdot CH_2\cdot OAc)_2$ , produced by the action of sodium acetate on methylene chlorhydrin, is a liquid boiling at

245—246°; it is soluble in water and in the ordinary organic solvents, and, dissolved in benzene, has the normal molecular weight.

In presence of aluminium chloride, dichlorotrioxymethylene and benzene condense, giving diphenylmethane, which is also obtained by the condensation of methylene chlorhydrin with benzene; these two, if dissolved in carbon bisulphide, and in presence of zinc chloride or zinc dust, give rise to benzylic chloride. T. H. P.

**Action of Potash on Epichlorhydrin in the Presence of Alcohols.** By V. ZUNINO (*Real. Accad. Linc.*, 1897, ii, 348—350).—With the method commonly employed for the preparation of the ethers of glycerol, which consists in treating dichlorhydrin with sodium alkyl oxides, the yield is small, owing to the occurrence of secondary reactions. Much better results are obtained by adding epichlorhydrin to the theoretical amount of the alcohol containing 10 per cent. of potassium hydroxide in solution, and in this way the following ethers were prepared, the figures indicating boiling points and specific gravities at 21°. Diethylic ether, 190—191°, 0.920; dimethylic ether, 169°, 0.915; dipropylic ether, 215—217°; diallylic ether, 225—227°, 0.991; di-isoamylic ether, 269—270°, 0.912. N. L.

**Lithiummethylammonium.** By HENRI MOISSAN (*Compt. rend.*, 1899, 128, 26—30).—When methylamine, free from ammonia, is liquefied in contact with sodium, potassium, or calcium, no combination takes place, and no blue solution is formed, even after prolonged contact, but with lithium, a deep blue solution is formed at once with development of heat. After remaining for some time at the ordinary temperature, the very thick and very dark blue liquid has the composition  $\text{NH}_2\text{MeLi}$ ,  $2\text{NH}_2\text{Me}$ , and is analogous to the compound formed by ammonia. When heated, or when placed in a vacuum, this liquid is decomposed and crystallised lithium is left, but no gas other than methylamine is liberated. If, however, the liquid is allowed to decompose until a small quantity of lithium is liberated, the compound  $\text{NH}_2\text{MeLi}$ , *lithiummethylammonium*, is obtained as a crystalline solid with a metallic lustre. It is stable at the ordinary temperature, but decomposes somewhat rapidly in a vacuum or when heated. When mixed with ether, it yields a blue solution stable at the ordinary temperature, but if an excess of ether is added, the blue colour disappears and a grey solid separates which is decomposed by water. Benzene and terebenthene decompose the lithiummethylammonium, and it reacts violently with carbon tetrachloride, chloroform, or ethylic iodide, combines with oxygen and nitrogen at the ordinary temperature, and is decomposed by cold water with liberation of hydrogen and methylamine, and formation of lithium hydroxide. C. H. B.

**Amines and Amides derived from Aldehydes.** By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1898, [vii], 15, 469—576).—This paper contains a discussion of the author's work on formaldehyde and hexamethylenetetramine, together with experimental details previously recorded. (Compare Abstr., 1896, i, 78, 519, 586, 637; 1897, i, 394, 456, 457, 504, 505, 586; ii, 87, 131, 359; 1898, i, 120, 362, 462, and this vol., i, 186, 234, 246; ii, 142.) G. T. M

**Preparation of Hydroxyethylamines.** By FELIX CHANCEL (*Compt. rend.*, 1899, 128, 313—314).—Contrary to Wurtz's statement (*Repert. chim.*, 1862, 42), a considerable quantity of trihydroxyethylamine hydrochloride is formed by acting on glycol chlorhydrin with warm, aqueous ammonia; the *aurichloride* of the base crystallises from water in monohydrated, golden leaflets and melts at 68°. The platinochlorides of both mono- and di-hydroxyethylamine crystallise with  $1\text{H}_2\text{O}$ , and are separated with difficulty; the normal *oxalate* of mono-hydroxyethylamine is a white substance which dissolves easily in water but sparingly in alcohol. W. A. D.

**Synthesis of Propanediolamines by the Action of Ammonia and Amines on Glycide.** By LUDWIG KNORR and EDUARD KNORR (*Ber.*, 1899, 32, 750—757).—1-Aminopropane-2:3-diol- ( $\gamma$ -amido-propylenic  $\alpha\beta$ -glycol),  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , is made by allowing a mixture of glycide (1 part) and 25 per cent. ammonia solution (100 parts) to remain for some hours at ordinary temperatures, and is isolated by fractional distillation, which is finally conducted under reduced pressure; aminodipropanediol and aminotripropanediol are also produced in small quantities. It forms a pale yellow, very viscid liquid having a faint basic odour; its aqueous solution is alkaline to litmus, and may be accurately titrated with methyl-orange. It is excessively hygroscopic, and absorbs carbonic anhydride with avidity. It boils and decomposes slightly at 264—265° under 739 mm. and at 238—239° under 325 mm. pressure, and has the following physical constants:—Refractive power  $n_D$  1.4900; sp. gr. 1.1752 at 20°/4°; molecular refraction  $M_{Na} = 22.39$ , the number calculated being 22.55. The substance has already been obtained by Chiari (this vol., i, 325) from acetyl dibromopropylamine, but the method is one of great practical difficulty. The *hydrochloride* is obtained as a viscid syrup, and the *aurichloride* as an orange-yellow, resinous precipitate; the *oxalate* crystallises from dilute alcohol in shining leaflets and melts at 69—74°; the *picrolonate*,  $\text{C}_3\text{H}_9\text{O}_2\text{N}\cdot\text{C}_{10}\text{H}_8\text{N}_4\text{O}_5$ , crystallises in rounded aggregates of prisms and melts and decomposes at 219—220°. A dilute aqueous solution of aminopropanediol yields white precipitates with mercuric chloride and potassium cadmium iodide, a yellow precipitate with potassium bismuth iodide, and a caseous, white precipitate with tannin; with platinic chloride, picric acid, and potassium mercuric iodide, no precipitates are formed.

$\gamma$ -Methylamidopropylenic  $\alpha\beta$ -glycol,  $\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ , is a colourless liquid which is viscid when cold but becomes mobile when hot, and boils at 235—250°. It is readily soluble in water and alcohol, sparingly soluble in ether, ethylic acetate, and acetone, and is insoluble in benzene. Its aqueous solution is strongly alkaline, and may be accurately titrated with methyl-orange as indicator. The free base rapidly absorbs carbonic anhydride and moisture. The *hydrochloride* is obtained as a viscid syrup. The *picrolonate*,  $\text{C}_4\text{H}_{11}\text{O}_2\text{N}\cdot\text{C}_{10}\text{H}_8\text{N}_4\text{O}_5$ , crystallises from alcohol in orange prisms and melts, after sintering slightly, at 212°; an *isomeric picrolonate* is obtained at the same time, and its formation probably indicates that

the production of the base is accompanied by that of  $\beta$ -methylamido-propylenic  $\alpha\beta$ -glycol.

$\gamma$ -Dimethylamidopropylenic  $\alpha\beta$ -glycol,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , obtained by the action of glycide on a solution of trimethylamine, is identical with the substance obtained by Roth (*Ber.*, 1882, 15, 1173) by the action of trimethylamine on monochlorhydrin. It is a colourless, viscid, hygroscopic, basic oil which dissolves more readily in ether and chloroform than do the corresponding amido- and methylamidoglycols. The *methiodide*,  $\text{C}_6\text{H}_{16}\text{NO}_2\text{I}$ , crystallises from absolute alcohol in characteristic shining, orange leaflets, and melts at  $133$ — $134^\circ$ ; the *picrolonate* separates from absolute alcohol in bright yellow, spherical aggregates, and melts without decomposing at  $160^\circ$ .

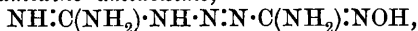
$\gamma$ -Ethylamidopropylenic  $\alpha\beta$ -glycol,  $\text{NEt} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , distils at  $145^\circ$  under a pressure of 25 mm. [Chiari (*loc. cit.*) gives  $141$ — $142^\circ$  under a pressure of 18 mm.], the *picrolonate* separates from absolute alcohol as a bright yellow, crystalline mass and decomposes at  $237^\circ$ .

$\gamma$ -Diethylamidopropylenic  $\alpha\beta$ -glycol,  $\text{NEt}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , boils at  $233$ — $235^\circ$  under 748 mm. pressure [Roth (*loc. cit.*) gives  $233$ — $235^\circ$ ]. The *picrolonate* crystallises from absolute alcohol in concentrically grouped, shining needles having a deep orange-yellow colour; it melts without decomposing at  $116$ — $118^\circ$ . A. L.

**Diazoamido-compounds of the Fatty Series.** By JOHANNES THIELE and WILHELM OSBORNE (*Annalen*, 1899, 305, 64—80).—*Diazoguanidine cyanide* (triazendicarbamidine nitrile or amidoimidomethylcyanotriazen),  $\text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{N} \cdot \text{N} \cdot \text{CN}$ , precipitated on mixing aqueous solutions of diazoguanidine nitrate and potassium cyanide, crystallises from water in small, yellow needles, which become brown above  $200^\circ$ , and melt indefinitely at higher temperatures, undergoing complete decomposition; the nitrate melts at  $123^\circ$ .

*Triazendicarbamidine amide*,  $\text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{N} \cdot \text{N} \cdot \text{CONH}_2$ , crystallises from hot water in yellow needles containing  $1\text{H}_2\text{O}$ , and detonates at  $139^\circ$  without fusing; the *hydrochloride* is obtained on heating diazoguanidine cyanide with hydrochloric acid at  $60$ — $70^\circ$ . The *nitrate* crystallises in lustrous needles, and explodes at  $136^\circ$ ; the *silver nitrate* compound,  $\text{C}_2\text{H}_6\text{N}_6\text{O} + \text{AgNO}_3$ , is exceedingly hygroscopic. Boiling water resolves the hydrochloride into guanidine, nitrogen, carbonic anhydride, and ammonia.

*Triazendicarbamidine amidoxime*,

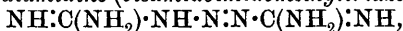


prepared from diazoguanidine cyanide and hydroxylamine, melts and decomposes at  $144^\circ$ ; ferrous sulphate develops a reddish-brown coloration in alkaline solutions, and boiling water resolves it into amido-tetrazole. The *nitrate* melts and explodes at about  $80^\circ$ , and the *hydrochloride* melts at  $163^\circ$ ; the sulphate dissolves with difficulty in cold water, and melts at  $179^\circ$ .

*Triazendicarbamidine imido-ether* is obtained in the form of *dihydrochloride*,  $\text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{NH} \cdot \text{N} \cdot \text{N} \cdot \text{C}(\text{OEt}) \cdot \text{NH}_2 \cdot 2\text{HCl}$ , by the action of hydrogen chloride on diazoguanidine cyanide in presence of ether and absolute alcohol; the salt melts at  $107$ — $110^\circ$ .

The *ethylic* salt of triazendicarbamidine (*ethylic* amidoimido-methyltriazencarboxylate),  $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{N}\cdot\text{N}\cdot\text{COOEt}$ , prepared from the dihydrochloride of the imido-ether by the action of sodium carbonate, crystallises from water, and melts at  $162^\circ$ ; the *hydrochloride* yields crystals containing  $1\text{H}_2\text{O}$ , and melts at  $155^\circ$ .

*Triazendicarbodiamidine* (*bisamidoimidomethyltriazene*),



is obtained in the form of carbonate when the hydrochloride of the imido-ether is treated with alcoholic ammonia, and afterwards with sodium carbonate; it contains  $1\frac{1}{2}\text{H}_2\text{O}$ , becomes dark yellow at  $150^\circ$ , and melts at  $165^\circ$ .  
M. O. F.

**Derivatives of Triazan (Prozan).** By JOHANNES THIELE and WILHELM OSBORNE (*Annalen*, 1899, 305, 80—96. Compare Abstr., 1898, i, 120).—*Ethylic* amidoimidosulphomethyltriazencarboxylate,  $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{N}(\text{SO}_3\text{H})\cdot\text{NH}\cdot\text{COOEt}$ , prepared by the action of sodium hydrogen sulphite on the amido-ether of triazendicarbamidine (foregoing abstract), crystallises from boiling water in slender, white needles, and melts at  $180^\circ$ . Boiling aqueous alkalis eliminate one-half the available nitrogen from the substance, whilst boiling with acids resolves it into nitrogen, carbonic oxide, ethylene, sulphuric acid, ammonia, carbonic anhydride, hydrazine, and guanidine. The *amide*,  $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{N}(\text{SO}_3\text{H})\cdot\text{NH}\cdot\text{CONH}_2$ , obtained by triturating the amide of triazendicarbamidine with sodium hydrogen sulphite, crystallises from water in small, white needles, and melts at  $141^\circ$ . Boiling caustic soda eliminates one-half of the nitrogen, sulphurous acid being also produced; boiling dilute sulphuric acid gives rise to sulphurous and formic acids, along with amidoguanidine. The *hydrochloride* crystallises with  $1\text{H}_2\text{O}$ , and melts at  $105^\circ$ .

When diazoguanidine cyanide is reduced at the ordinary temperature, with zinc dust and acetic acid, amidoguanidine is produced; the *ethylic* salt of triazendicarbamidine yields guanidine and *ethylic* hydrazinecarboxylate. At the ordinary temperature, the amide of triazendicarbamidine gives rise to guanidine and semicarbazone; at  $0^\circ$ , there is formed an unstable compound probably having the constitution  $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{NH}\cdot\text{NH}\cdot\text{CONH}_2$ , but which undergoes decomposition even at low temperatures.  
M. O. F.

**Acetyl Derivatives of Hydrazine.** By ROBERT STOLLÉ (*Ber.*, 1899 32, 796).—Di-, tri-, or tetra-acetylhydrazine can be prepared by heating hydrazine hydrate with 3, 4, or 5 mols. of acetic anhydride respectively.

*Diacetylhydrazine*,  $\text{NHAc}\cdot\text{NHAc}$ , crystallises from hot alcohol in crusts, melts at  $138^\circ$ , and boils at  $209^\circ$  under 15 mm. pressure, and is readily soluble in water, sparingly so in chloroform, and almost insoluble in ether, benzene, and light petroleum.

*Triacetylhydrazine*,  $\text{NAc}_2\cdot\text{NHAc}$ , is a colourless syrup; it boils at  $180$ — $183^\circ$  under 15 mm. pressure, and is soluble in alcohol and ether, but seems to decompose on solution in water.

*Tetraacetylhydrazine*,  $\text{NAc}_2\cdot\text{NAc}_2$ , separates from its solution in alcohol and ether in large crystals, or from ether in needles; it melts at

85°, boils at 141° under 15 mm. pressure, and decomposes at 300—350° under ordinary pressure into acetic anhydride and dimethylfurodiazole.  
J. F. T.

**Electrolytic Preparation of Dithionbisulphides.** By CARL SCHALL and S. KRASZLER (*Zeit. Elektrochem.*, 1898, 5, 225—226. Compare Schall, *Abstr.*, 1897, i, 317).—The electrolysis of aqueous solutions of potassium methyl-, isobutyl-, or isoamyl-xanthates yields the corresponding bisulphides at the anode. When an aqueous solution of diethylammonium diethyldithiocarbamate is electrolysed, a deposit of tetrethylthiuram bisulphide,  $S_2(CS \cdot NEt_2)_2$ , is formed on the anode, whence it is washed by ether. The anodic deposit obtained from potassium phenylthiocarbazide,  $NHPh \cdot NH \cdot CS \cdot SK$ , consists of diphenylthiocarbazide,  $CS(NH \cdot NHPh)_2$ . An aqueous solution of potassium ethyltrithiocarbonate,  $SEt \cdot CS \cdot SK$ , yields the hitherto unknown dithionbisulphide,  $S_2(CSEt)_2$ , in the form of a yellow, uncrystallisable oil which readily decomposes. With aniline, it yields thiocarbaniide, sulphur, mercaptan, and hydrogen sulphide; phenylthiocarbimide was also found, probably owing to the intermediate formation of phenyldithiourethane.  
T. E.

**Compounds of Aldehydes with Mercuric Sulphate.** By GEORGES DENIGÈS (*Compt. rend.*, 1899, 128, 429—431).—Acetaldehyde yields the compound  $SO_4 \cdot (HgO)_2 \cdot Hg \cdot C_2H_4O$ , which always contains a little mercurous sulphate, but formaldehyde does not form a similar compound, and simply reduces the mercuric salt to mercurous sulphate, the latter separating in a well crystallised form. This behaviour of the lowest homologue is analogous to that of ethylene and benzene, which likewise do not form compounds with mercuric sulphate. (Compare *Abstr.*, 1898, i, 546, 618, and this vol., i, 22, and ii, 256.)  
C. H. B.

**Chloral-ammonia.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1898, [iii], 19, 171—173. Compare *Abstr.*, 1898, i, 462).—The molecular weight of this compound, determined by the cryoscopic method in glacial acetic acid, indicates a non-associated molecule; in benzene and ethylenic dibromide, it corresponds with the doubled formula.  
G. T. M.

**Methyloctenonal.** By GEORGES LÉSER (*Compt. rend.*, 1899, 128, 371—373).—The methyloctenonal previously described (this vol., i, 330) is very stable, boils without decomposing at 108—110° under 10 mm. pressure, and solidifies on cooling; under ordinary pressure, it boils at 205—210° and decomposes slightly. With hydroxylamine, it yields an isoxazole which boils at 113—114° under 16 mm. pressure, and reacts very energetically with sodium ethoxide, yielding a nitrile,  $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CN$ , of the same percentage composition, which boils at 123—124° under a pressure of 16 mm., and when heated with alcoholic potash is converted into methylhexenamide (nacreous crystals melting at 85—86°), or by prolonged action into methylhexenoic acid, boiling at 216—218°. The ethyl derivative of the nitrile  $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CN$ , when



heated with alcoholic potash, yields ammonia, formic acid, and methyl-nonenone boiling at 203—205° (compare this vol., i, 190).

Methyloctenonal forms an anilide which boils at 210—212° under 20 mm. pressure, and yields a crystallisable base when treated with concentrated sulphuric acid. With methylaniline, however, it forms a compound,  $C_{16}H_{21}NO$ , which boils at 214—216° under 17 mm. pressure, and this reaction, as well as others, can only be explained by assuming that methyloctenonal is tautomeric, and sometimes behaves as if it has the constitution  $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH \cdot CH \cdot OH$ , although generally its behaviour corresponds with the constitution  $CMe_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CHO$ .  
C. H. B.

**A Reaction of Aldehydes and Ketones.** By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Bull. Soc. Chim.*, 1898, [iii], 19, 134—137. Compare Abstr., 1897, ii, 470).—The use of aldehydes and ketones for increasing the reducing power of organic developers has already been studied by the authors, and the reaction is now proposed as a delicate test for compounds of the aldehydic or ketonic type. To apply the test, 25 c.c. of an aqueous (or alcoholic) solution of the substance under examination is mixed with 50 c.c. of an aqueous solution of sodium sulphite (7 per cent.) and pyrogallol (1.5 per cent.), or of sodium sulphite (20 per cent.), and quinol (2 per cent.), and the action of the liquid on a photographic plate is compared with that of 50 c.c. of the same test-solution to which 25 c.c. of water (or alcohol) has been added. In this way, it is possible to detect the presence of 1 in 25,000 of formaldehyde, 1 in 15,000 of acetaldehyde, and 1 in 2500 of acetone. The reaction is not, however, of universal application, since it is not given by paraldehyde, chloral, diketones, ketonic acids, ketonic alcohols, aromatic ketones, or by aromatic aldehydes other than those of simple function or those in which the other functions are of a neutral character.  
N. L.

**Action of Ammonia on Dithioacetylacetone.** By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1898, [iii], 19, 246—249).—On passing gaseous ammonia into, or mixing alcoholic ammonia with, an ethereal solution of dithioacetylacetone, the *additive* compound,  $C_{10}H_{14}S_2O_4 \cdot 2NH_3$ , separates as a light-yellow, crystalline powder, which decomposes in the air, or on adding dilute acids, to form dithioacetylacetone; when the additive compound is left in a closed vessel, or is gently warmed on the water-bath, it loses water and yields yellow crystals having the composition  $C_{10}H_{16}N_2S_2O_2$ , which darken, when heated, at 120° and melt and decompose at 160°. The compound so obtained does not yield a metallic derivative when treated with copper acetate (compare Abstr., 1895, i, 168), and therefore probably has the constitution  $S_2(CAc \cdot CMe \cdot NH_2)_2$  rather than  $S_2(CHAc \cdot CMe \cdot NH)_2$ ; this view is in accord with the fact that the similar derivative of acetylacetone has the constitution  $NH_2 \cdot CMe \cdot CHAc$ , although that obtained from methylacetone appears to have the structure  $CH_3 \cdot CHAc \cdot CMe \cdot NH$  (A. and C. Combes, Abstr., 1893, i, 454).

On adding alcoholic methylamine to an ethereal solution of dithio-

acetylacetone, a light yellow, crystalline *additive* compound separates, which decomposes in the air, dithioacetylacetone being regenerated.

W. A. D.

**Decomposition of Ferric Acetate.** By W. HERZ (*Zeit. anorg. Chem.*, 1899, 20, 16—20).—A pure neutral solution of ferric acetate can be evaporated to dryness on the water-bath without decomposition. If the solution is heated in a water-bath for 10 hours, a decomposition takes place and basic acetate and ferric hydroxide are formed. At the ordinary temperature, the solution is stable for weeks, but if impurities are present a yellow precipitate is quickly formed. At 44°, a reversible reaction takes place, as expressed in the equation  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 \cdot \text{C}_2\text{H}_3\text{O}_2 + 2\text{C}_2\text{H}_4\text{O}_2$ , and the liberated acetic acid has a catalytic action, which at first accelerates the decomposition.

E. C. R.

**Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Ethylic Sodiomalonnate.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.* 1898, [iii], 19, 78—80).—On gradually adding ethylic chloroglyoxylate (1 mol.) to ethylic sodiomalonnate suspended in ether, and subsequently distilling under a pressure of 10 mm., two fractions are obtained boiling at 140° and 220° respectively; the second of these is the larger, and consists of *ethylic carboxyoxalacetate*,  $\text{CH}(\text{COOEt}) \cdot \text{CO} \cdot \text{COOEt}$ , whilst the first consists of triethylic methanetricarboxylate, formed, together with carbonic oxide, by the decomposition of the product of higher boiling point.

When phenylhydrazine (1 mol.) is added to ethylic carboxyoxalacetate, it gives rise, not to the expected pyrazole derivative,  $\text{C}(\text{COOEt})=\text{N} \cdot \text{CH}(\text{COOEt}) \cdot \text{CO} > \text{NPh}$ , but to ethylic malonnate, together with the phenylhydrazide,  $\text{COOEt} \cdot \text{CO} \cdot \text{N}_2\text{H}_2\text{Ph}$ , of monethylic oxalate, melting at 113° (Bulow, Abstr., 1887, 138); it thus appears that, in this case, an acid is formed by hydrolysis, phenylhydrazine initially acting in the same manner as alkalis. This behaviour is similar to that which occurs in the case of ethylic brom- and dibrom-oxalacetates, which are decomposed by phenylhydrazine, although ethylic oxalacetate yields a normal derivative; the influence of the  $\text{COOEt}$ -group in diminishing stability is thus similar to that of a halogen. Ethylic carboxyoxalacetate is slowly decomposed by moisture, giving rise to oxalic acid.

W. A. D.

**Ethylic Methylenemalonate.** By GUSTAV KOMPPA (*Chem. Centr.*, 1898, ii, 1169; from *Oefversigt af Finska Vet.-Soc. Förhandlingar*, 40).—From the products of the action of diethylamine and formaldehyde on ethylic malonnate, the author has isolated, not only ethylic methylenedimalonnate,  $\text{CH}_2[\text{CH}(\text{COOEt})_2]_2$ , but also a polymeride identical with the compound which Zelinsky (Abstr., 1890, 364) obtained by the action of sodium ethoxide on methylenic iodide and ethylic malonnate. It is best prepared by allowing a mixture of ethylic malonnate (1 mol.) with formaldehyde (1 mol.) and diethylamine to remain at the ordinary temperature for several days, then separating

the oil and distilling in a vacuum. The fraction which boils at 140—200° under 25 mm. pressure forms an amorphous mass of the polymeride, which is easily soluble in hot alcohol, chloroform, and benzene. By distilling the oil under the ordinary pressure, ethylic methylenemalonate is obtained, which only changes to the polymeride after some time. *Ethylic dibromomethylenemalonate*,  $\text{CH}_2\text{Br}\cdot\text{CBr}(\text{COOEt})_2$ , prepared by adding bromine to ethylic methylenemalonate, boils at 130—140° under 5 mm. pressure, with liberation of some hydrogen bromide. E. W. W.

**A New Additive Action of Alkylenic Oxides.** By WILHELM TRAUBE and E. LEHMANN (*Ber.*, 1899, 32, 720—721).—When ethylic sodiomalonate, suspended in absolute alcohol, is treated with ethylenic oxide, it yields the sodium derivative of a colourless oil which, under the influence of alcoholic ammonia, is converted into the *amide*,  $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$ , of hydroxyethylmalonic acid; the substance crystallises in colourless needles, and melts at 150°. Ethylenic oxide also acts on ethylic sodioacetoacetate.

*Chlorohydroxypropylmalonamide*,  $\text{C}_6\text{H}_{11}\text{ClN}_2\text{O}_3$ , obtained by treating with alcoholic ammonia the product of the action of epichlorhydrin on ethylic sodiomalonate, separates from absolute alcohol in colourless crystals, and melts at 117—118°. M. O. F.

**Transformation of Unsaturated Acids. Hexylaticonic Acid.** By RUDOLPH FITTIG and EMIL STUBER (*Annalen*, 1899, 305, 1—18).—Hexylaticonic acid is obtained by the action of a boiling 20 per cent. solution of caustic soda on hexylitaconic acid (compare Fittig and Hoeffken, this vol., i, 339); it crystallises in transparent nodules and in minute needles from ether and benzene respectively, and melts at 78—78·5° (compare Fittig, *Abstr.*, 1893, i, 692). The *barium* and *calcium* salts contain  $\frac{1}{2}\text{H}_2\text{O}$ , and the *silver* salt, which is amorphous, rapidly becomes violet-brown when exposed to light. *Bromohexylisoparaconic acid*,  $\text{C}_{11}\text{H}_{17}\text{BrO}_4$ , obtained by treating hexylaticonic acid with a solution of bromine in chloroform, crystallises from carbon bisulphide in lustrous, transparent needles, which melt and decompose at 134—135°; it is insoluble in cold water, but dissolves in water at 70—80°, from which it crystallises in thin, white needles melting at 145—146°.

*Hexylisoparaconic acid*,  $\text{C}_{11}\text{H}_{18}\text{O}_4$ , prepared by reducing bromohexylisoparaconic acid in dilute sulphuric acid with 4 per cent. sodium amalgam, crystallises from benzene in lustrous leaflets, and melts at 83—84°; the *calcium* and *silver* salts are anhydrous.

*Hexylisaconic acid*,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , obtained from bromohexylisoparaconic acid by the action of caustic soda, crystallises from a mixture of ether and petroleum in lustrous plates, and melts at 57·5—58·5°; reduction with sodium amalgam converts it into hexylisoparaconic acid. The *calcium* salt crystallises in long, slender needles containing  $3\text{H}_2\text{O}$ ; the *silver* salt is amorphous, and slowly becomes violet under the influence of light. The *acid*,  $\text{C}_{11}\text{H}_{18}\text{O}_5$ , is also produced when bromohexylisoparaconic acid is treated with caustic soda, being separated from hexylisaconic acid by the comparatively sparing solubility of the calcium salt; the authors regard it as ketoheptylsuccinic acid, but this point

remains undecided. It crystallises from the aqueous solution in nodules, and melts at  $99-99.5^\circ$ ; the *barium* salt contains  $1\text{H}_2\text{O}$ , and the *calcium* salt is anhydrous. The *acid*,  $\text{C}_{11}\text{H}_{18}\text{O}_4$ , obtained by reducing the foregoing acid with sodium amalgam, crystallises in leaflets, and melts at  $72-72.5^\circ$ .

*Undecodilactone*,  $\text{C}_{11}\text{H}_{16}\text{O}_4$ , produced on heating bromohexylisoparaconic acid with water in a reflux apparatus, crystallises from a mixture of ether and petroleum in white nodules and melts at  $66-67^\circ$ ; hexylisaconic acid is formed at the same time, and in much greater amount.

The *dibromide* of hexylitaconic acid,  $\text{C}_{11}\text{H}_{18}\text{Br}_2\text{O}_4$ , prepared by the action of bromine in chloroform on hexylitaconic acid, crystallises from a mixture of ether and petroleum and melts at  $134-135^\circ$ .

M. O. F.

**Oxidation of Unsaturated Dibasic Acids.** By RUDOLPH FITTIG and WILHELM KÖHL (*Annalen*, 1899, 305, 41—52).—When itaconic acid is oxidised with an alkaline solution of potassium permanganate, itatartaric and hydroxyparaconic acids are produced. *Hydroxy-*

*paraconic acid*,  $\text{COOH}\cdot\text{C}(\text{OH})\begin{matrix} \text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{O} \end{matrix}$ , crystallises from carbon tetrachloride and melts at  $104^\circ$ . The *calcium* salt, which contains  $2\text{H}_2\text{O}$ , has been described by Morawski; the *barium* and *silver* salts are anhydrous.

Oxidation of citraconic and mesaconic acids gives rise to oxalic and pyruvic acids; phenylitaconic and phenylitaconic acids yield benzaldehyde along with malonic and oxalic acids.

M. O. F.

**Oxidation of Isobutylitaconic, Isobutylcitraconic, and Isobutylmesaconic Acids.** By RUDOLPH FITTIG and FRIEDRICH KAEHLBRANDT (*Annalen*, 1899, 305, 52—63).—When isobutylitaconic acid is oxidised with an alkaline solution of potassium permanganate, it yields valeraldehyde along with malonic and oxalic acids; isobutylcitraconic and isobutylmesaconic acids give rise to oxalic, isocaproic, and isobutylpyruvic acids.

*Isobutylpyruvic acid*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$ , forms a crystalline mass which melts at  $22^\circ$ ; it deliquesces when exposed to moist air, and is readily volatile in steam. The *calcium* salt contains  $2\text{H}_2\text{O}$ , and the *barium* salt  $1\text{H}_2\text{O}$ ; the *silver* salt crystallises from warm water, and is sensitive to light. The *phenylhydrazone* crystallises from a mixture of ether and petroleum in aggregates of needles, and melts at  $105^\circ$ .

M. O. F.

**Optically Active  $\alpha$ -Methylmalic Acid (2-Methyl-2-butanoldioic Acid).** By WILHELM MARCKWALD and S. AXELROD (*Ber.*, 1899, 32, 712—716. Compare Schütz and Marckwald, *Abstr.*, 1896, i, 203).—The authors have obtained optically active  $\alpha$ -methylmalic (citramalic) acid from the racemic substance by the agency of brucine. The interest of this observation lies in the fact that the optically active compounds hitherto described have invariably contained one atom of hydrogen directly united with the asymmetric carbon atom.

*d-Citramalic acid* melts at  $95^\circ$ , and is extremely hygroscopic,

whereas the racemic compound melts at  $119^{\circ}$ , and is not hygroscopic; a 74 per cent. solution has the specific rotatory power  $[\alpha]_D 34.67^{\circ}$ . The *brucine* salt dissolves readily in hot water, but is only sparingly soluble in cold.

The specific rotations of citramalic acid and the sodium salt have been recorded for various concentrations and wave-lengths.

M. O. F.

**Synthesis of Terebic Acid.** By EDMOND E. BLAISE (*Bull. Soc. Chim.*, 1898, [iii], 19, 275—277).—Attempts to prepare terebic acid by the synthetical method suggested by Reformatsky, which consists in the condensation of acetone with ethylic bromosuccinate in the presence of metallic zinc, decomposition of the zinc compound thus produced with water, and hydrolysis of the ethylic diaterebate obtained, were unsuccessful, but on substituting a zinc-copper couple for the zinc, a product was readily obtained which was identified as terebic acid by analysis and by its conversion, on distillation, into 2-methyl-pentanolide. The yield is small (10 to 15 grams for every 100 grams of ethylic bromosuccinate employed) but much better than that obtained in the preparation of the acid by the oxidation of pinene. N. L.

**Hydroxytrimethylsuccinic Acid and its Derivatives.** By GUSTAV KOMPPA (*Chem. Centr.*, 1898, ii, 1168—1169; from *Acta. Soc. Scient. Fennicæ*, 24, 1—14). A good yield of hydroxytrimethylsuccinic acid,  $\text{COOH} \cdot \text{CMe}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{COOH}$ , is obtained by adding hydrochloric acid in small portions to a cooled mixture of powdered potassium cyanide with ethylic dimethylacetoacetate dissolved in ether. After remaining in a closed vessel for a week, the ethereal layer is poured off and mixed with twice its volume of concentrated hydrochloric acid; the mixture, after remaining 24 hours at the ordinary temperature, is heated on the water bath for a day and then evaporated. Hydroxytrimethylsuccinic acid separates from water or ethylic acetate in clear, rhombic crystals and melts at  $155$ — $159^{\circ}$ , the exact temperature depending on the rapidity of heating; if the acid is kept, its melting point gradually sinks. The properties of the acid render somewhat doubtful its identity with Tiemann's hydroxytrimethylsuccinic acid, obtained by the oxidation of pinene and with Kachler's acid prepared by the oxidation of camphor. It dissolves easily in water, alcohol, and hot ethylic acetate, is rather soluble in ether, slightly so in benzene and light petroleum, and is precipitated by copper sulphate, ferric chloride, and lead nitrate. The ammonium salt crystallises in flat needles and is very easily soluble in water; the silver salt,  $\text{C}_7\text{H}_{10}\text{O}_5\text{Ag}_2$ , is a white, amorphous substance insoluble in water; the calcium salt,  $\text{C}_7\text{H}_{10}\text{O}_5\text{Ca} + \frac{1}{2}\text{H}_2\text{O}$ , does not dissolve in water unless allowed to remain with it for a long time, when a solution is obtained which, on evaporation, yields a brittle, glassy mass. *Hydroxy-*

*trimethylsuccinanil*,  $\begin{array}{c} \text{CMe}_2 \text{---CO} \\ | \\ \text{CMe}(\text{OH}) \cdot \text{CO} \end{array} \text{>NPh}$ , prepared by boiling the acid with aniline, crystallises from dilute alcohol in small needles, melts at  $145^{\circ}$ , is easily soluble in most solvents, and slightly soluble in water and light petroleum. The corresponding *paratolil*,  $\text{C}_{14}\text{H}_{17}\text{O}_4\text{N}$ , crystallises from alcohol in needles, melts at  $185^{\circ}$ , and with acetic chloride

yields an *acetyl* derivative,  $C_{16}H_{19}O_4N$ , which crystallises from hot alcohol in flat needles, melts at  $131^\circ$ , and is slightly soluble in cold alcohol. *Acetylhydroxytrimethylsuccinic anhydride*,  $C_9H_{12}O_5$ , obtained by the prolonged action of acetic chloride on hydroxytrimethylsuccinic acid, crystallises from light petroleum in needles and melts at  $68^\circ$ ; in this reaction, a compound of unknown composition is also formed, this melts at  $142^\circ$  and is insoluble in light petroleum. By the action of alcohol and hydrochloric acid, only a portion of hydroxytrimethylsuccinic acid is converted into the ethylic salt, which is better prepared by the action of ethylic iodide on the silver salt; it is a liquid which boils at  $122$ — $123^\circ$  under 9 mm. pressure and has a sp. gr. of 1.066 at  $18^\circ$ . *Ethylic chlorotrimethylsuccinate*,  $COOEt \cdot CMe_2 \cdot CMeCl \cdot COOEt$ , prepared by heating at  $83^\circ$  a mixture of phosphorus pentachloride with hydroxytrimethylsuccinic acid dissolved in chloroform, boils at  $114.5$ — $115.5^\circ$  under 12 mm. pressure, and when hydrolysed with hydrochloric acid, yields an acid which does not contain chlorine and is probably a  $\beta$ -lactone-carboxylic acid. By the action of phosphorus pentabromide on hydroxytrimethylsuccinic acid, a complex mixture is obtained, the presence of the alkyl groups apparently rendering the hydroxyl group more difficult to replace. E. W. W.

**Condensations with Ethylic  $\beta$ -Chlorisovalerate.** By CLEMENTE MONTEMARTINI (*Gazzetta*, 1898, 28, ii, 305—312).—The author has succeeded in verifying the constitution assigned by him to the acid obtained by the action of chlorine on isovaleric acid (*Abstr.*, 1898, i, 236). On heating the ethylic salt of the chlorinated acid in a closed tube with alcohol and potassium cyanide, cyanogen is substituted for the chlorine atom, and on hydrolysing the product by means of hydrochloric acid, asymmetrical dimethylsuccinic acid is obtained. The chlorine atom in the chlorisovaleric acid must therefore be in the  $\beta$ -position.

Ethylic malonate and ethylic  $\beta$ -chlorisovalerate when heated together with sodium ethoxide, give a condensation product which on hydrolysis with alcoholic potash yields for the most part  $\beta\beta$ -dimethylglutaric acid, and probably is a derivative of the tribasic acid,  $COOEt \cdot CH_2 \cdot CMe_2 \cdot CH(COOEt)_2$ . T. H. P.

**Formation of Carbamides.** By AD. JOUVE (*Compt. rend.*, 1899, 128, 114—115).—When a solution of carbonic oxide in ammoniacal cuprous chloride is heated at  $105^\circ$  under pressure for five or six hours, carbamide is formed and copper separates:  $CO + 2NH_3 = CO(NH_2)_2 + H_2$  and  $Cu_2Cl_2 + H_2 = Cu_2 + 2HCl$ . Amines of the methane and benzene series behave in the same manner; aniline, for example, yields diphenylcarbamide. C. H. B.

**Oxidation of some Carbamides.** By WILLIAM CECIL SNIDER DE CONINCK (*Compt. rend.*, 1899, 128, 365—366).—The author has investigated the oxidation of several carbamides by a mixture of normal potassium chromate and sulphuric acid in place of the ordinary chromic mixture. Carbamide yields a small quantity of free nitrogen in addition to carbonic anhydride. Thiocarbamide yields ammonium thiocyanate and, consequently, thiocyanic acid and the products of its

decomposition, together with ammonium sulphate and ammonium hydrogen sulphate, and in some cases small quantities of free nitrogen. Phenylthiocarbamide, diphenylthiocarbamide, methylcarbamide, phenylcarbamide, and diphenylcarbamide do not yield free nitrogen and the diphenyl derivatives are less readily oxidised than the monophenyl derivatives. Benzylcarbamide is oxidised with difficulty, and yields, amongst other products, ammonium sulphate and a small quantity of benzylcarbimide. Phenylcarbamide yields sulphanilic acid and benzonitrile, as well as carbonic anhydride. C. H. B.

**Action of Zinc on Ethylic Bromisobutyrate and Furfuraldehyde.** Synthesis of  $\beta$ -Furfuryl- $\alpha$ -dimethylethylenelactic Acid. By G. DAÏN (*Chem. Centr.*, 1898, i, 884; from *J. russ. chem. Ges.*, 29, 666—671).—*Ethylic  $\beta$ -furfuryl- $\alpha$ -dimethylethylenelactate*, prepared by dropping a mixture of 95 grams of ethylic bromisobutyrate and 50 grams of furfuraldehyde on to granulated zinc in an apparatus filled with carbonic anhydride, and allowing the product to remain in the dark for 10 days, separates from the fraction boiling at 267—277° in leaflets and sublimes at 293—296° without melting, forming needles. The sodium salt,  $\text{NaC}_9\text{H}_{11}\text{O}_4$ , separates in small, colourless crystals and the calcium salt,  $\text{Ca}(\text{C}_9\text{H}_{11}\text{O}_4)_2 + 3\frac{1}{2}\text{H}_2\text{O}$ , in small, crystalline granules; the barium salt is hygroscopic and easily soluble in alcohol.

E. W. W.

**Pyrone Group. V. Action of Iodic Acid on Pyromeconic Acid.** By ALBERTO PERATONER and G. LEONARDI (*Gazzetta*, 1898, 28, ii, 297—305).—No definite compounds could be isolated as the result of the action of iodic acid on meconic and comenic acids, but with pyromeconic acid, iodic acid gives iodopyromeconic acid,  $\text{C}_5\text{H}_3\text{O}_3\text{I}$ , and pentiodacetone in the cold, the latter alone being obtained if the solutions are boiling; in both cases, a copious evolution of carbonic anhydride takes place. The pentiodacetone, when decomposed with caustic soda, gave iodoform, sodium carbonate, and sodium iodide in the proportions required by the equation:  $\text{C}_5\text{H}_3\text{O}_3\text{I} + 4\text{NaOH} = \text{CHI}_3 + \text{Na}_2\text{CO}_3 + 2\text{NaI} + \text{H}\cdot\text{CHO} + \text{H}_2\text{O}$ ; formaldehyde was also formed, but no formic acid, the decomposition thus differing from those of the other haloid derivatives of acetone examined by Cloëz. These results do not lead to any definite conclusions as to the position of the substituent groups of the pyrone nucleus in pyromeconic acid. The authors have repeated Brown's experiments (*Annalen*, 1854, 92, 321) on the action of iodine chloride on pyromeconic acid, but obtained iodoform only, and not the compound to which he assigned the formula  $\text{C}_3\text{H}_4\text{O}_3\text{I}_8$ . T. H. P.

**Trimethylene from Trimethylenic Bromide.** By GABRIEL GUSTAVSON (*Compt. rend.*, 1899, 128, 437—438).—Trimethylene, prepared by the action of zinc powder and alcohol on carefully purified trimethylenic bromide boiling at 164·5—165°, is almost completely free from propylene. Wolkoff and Menshutkin's conclusion that trimethylene prepared in this way contains about 40 per cent. of propylene, is due to the facts that trimethylenic bromide frequently contains propylenic bromide and that the direct action of trimethylene on

bromine (in which Wolkoff and Menshutkin absorbed the gas) produces a mixture of trimethylenic bromide and propylenic bromide even when the trimethylene is pure. C. H. B.

**Conversion of Trimethylene into Propylene.** By SIMEON M. TANATAR (*Ber.*, 1899, 32, 702—705. Compare *Abstr.*, 1896, i, 457).—The author describes in some detail the experiments which led him to adhere to the original statement regarding the conversion of trimethylene into propylene (*loc. cit.*), in spite of the criticisms of Wolkoff and Menshutkin (this vol., i, 196). M. O. F.

**Constitution and Origin of Naphthenes.** By BRUNO BRUHN (*Chem. Zeit.*, 1898, 22, 900—902).—The author points out that the formation of benzene derivatives from the naphthenes by the action of various reagents is not a proof that these hydrocarbons are derivatives of benzene. Thus the formation of trinitrometaxylene from octonaphthene or of tribromopseudocumene from nononaphthene may be readily explained if it is supposed that these hydrocarbons are derivatives of pentamethylene, and that under the influence of the reagents the ring of five carbon atoms is broken and a new ring of six carbon atoms formed from the chain thus produced. The fact that the most stable saturated ring,  $C_nH_{2n}$ , consists of five carbon atoms whilst the most stable unsaturated ring,  $C_nH_n$ , contains six carbon atoms is in favour of this view. The new constitution of the naphthenes also agrees much better with the physical properties of these hydrocarbons, as expressed in the curve of boiling points and specific gravities (Markownikoff, *Annalen*, 1898, 301, Anh.). According to Engler's theory, the naphthenes have probably been produced from fatty acids resulting from the hydrolysis of glycerides, and in these circumstances compounds containing the stable five-membered ring would presumably be produced. The naphthenecarboxylic acids are probably formed in a similar manner, a portion of the oxygen being present in the ring.

A. H.

**Derivatives of Hexahydrometatoluic Acid (1 : 3-Methylcyclohexanecarboxylic Acid).** By W. SERNOFF (*Chem. Centr.*, 1898, i, 498—499; from *J. russ. chem. Ges.*, 29, 482—488).—Hexahydrometatoluic acid boils at 239—241°, and does not solidify at a very low temperature. By the action of bromine and red phosphorus, it forms the anhydride of the bromine derivative, which does not solidify on cooling, but after remaining with water for 24 hours and evaporating in a desiccator, yields heavy, monoclinic plates of the  $\alpha$ -bromo-acid,  $CH_2 \begin{smallmatrix} CH_2-CH_2 \\ | \quad | \\ CHMe \cdot CH_2 \end{smallmatrix} > CBr \cdot COOH$ , which melts at 118°. By heating the bromanhydride with formic acid (1 : 2), the  $\beta$ -bromo-acid,  $CH_2 \begin{smallmatrix} CH_2-CH_2 \\ | \quad | \\ CMeBr \cdot CH_2 \end{smallmatrix} > CH \cdot COOH$ , is obtained; it crystallises in triclinic prisms or plates, and melts at 142°. Both acids, when reduced with sodium amalgam, form an oil which, when treated with phosphorus pentachloride and then with aniline, yields the same anilide; this melts at 116°, whilst the anhydride of the original acid melts at 121—122°, and after recrystallising, or by



heating with hydrochloric acid, yields a product which melts at 124°. The author regards the hexahydro-acid obtained by reducing the bromo-acids as one of the isomerides contained in the ordinary hydrogenated acid. By heating the  $\alpha$ -bromo-acid with quinoline for an hour at 100°, it loses bromine, and forms an unsaturated liquid acid; this dissolves in water, and easily in light petroleum, decolorises potassium permanganate, and absorbs bromine in carbon bisulphide solution. When heated in alkaline solution on the water-bath, it yields an isomeride, which may also be prepared by removing bromine from the  $\alpha$ -bromo-acid; it crystallises from acetone in leaflets or needles, melts at 60—61°, and has the formula  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix} \text{C} \cdot \text{COOH}$ . The unsaturated acid, obtained by heating the  $\beta$ -bromo-acid with quinoline at 160—180° for 2 hours, when warmed in alkaline solution at 100°, yields a compound melting at 60—61°, and apparently identical with the compound obtained from the  $\alpha$ -acid, but in this case a non-crystallisable acid is formed by heating with alcoholic sodium hydroxide.

E. W. W.

**$\Delta^1$ -Cycloheptenecarboxylic Acid.** By EDUARD BUCHNER (*Ber.*, 1899, 32, 705—707. Compare *Abstr.*, 1898, i, 301).—Attention has been drawn (*loc. cit.*) to the similarity between suberenecarboxylic ( $\Delta^1$ -cycloheptenecarboxylic) acid and Einhorn and Willstätter's  $\Delta^1$ -1-ethylcyclopentene-4-carboxylic acid. Although the amides of these two acids melt at 126° and 130—131° respectively, they are regarded as identical by Willstätter (this vol., i, 26); the author considers it more probable, however, that Einhorn and Willstätter's acid is a cycloheptenecarboxylic acid having the ethylenic group in a different position.

M. O. F.

**Properties of Naphthenates and their Qualitative Distinction from Salts of Fatty Acids.** By K. CHARITSCHKOFF (*Chem. Centr.*, 1898, i, 1191—1192; from *J. russ. chem. Ges.*, 29, 691—696).—Naphthenic acids, according to Holde, are obtained by heating neutral petroleum with air in presence of alkali, and Lissenko and Zalosetzky have shown that small quantities are formed when petroleum is distilled. As separated from the crude distillate, these acids have a sp. gr. of 0.961 at 20°, distil without decomposing under 100 mm. pressure, and after repeated distillation are colourless and almost odourless. Although they have the composition of unsaturated compounds, they do not unite with bromine or hydrogen haloids. They dissolve in concentrated sulphuric acid with slight development of heat, and are charred by it after a time. They combine readily with sulphur, especially when warmed, but the sulphur is easily removed by alkali and alcohol. The salts, with the exception of the calcium salt, which crystallises in a fibrous mass, are amorphous; the alkali and silver salts are insoluble in hydrocarbons, the former being easily soluble, but the latter only very slightly so in water; the salts of the alkaline earths are insoluble in hydrocarbons and very slightly soluble in water; those of the heavy metals and of aluminium are very slightly soluble in water, but soluble in hydrocarbons, the iron and copper salts being the most soluble and

the zinc salt dissolving in 20 parts of hydrocarbon. The solution of the faintly blue copper salt in benzene has the intense green colour which is characteristic of the hydrates of copper salts and the white zinc, lead, and mercury salts give a faint yellowish tint to benzene; the last traces of benzene or light petroleum can only be removed from the salts with difficulty, probably on account of the formation of molecular compounds. The solubility of the copper salt in benzene affords a very delicate test for naphthenic acids and their salts, which are often used to adulterate cheap soaps, the copper salt being precipitated with copper sulphate, shaken with benzene, and estimated colorimetrically; small quantities of the copper salts of the fatty acids, however, are also dissolved by the benzene. The copper salts are strong disinfectants, and their use for impregnating wood has been suggested.

E. W. W.

#### Action of Potassium Persulphate on Aromatic Hydrocarbons.

By C. MORITZ and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 432—434).—When toluene (2 mols.) is heated with potassium persulphate (1 mol.) in a reflux apparatus at 100° for 3—4 hours, the mixture being stirred constantly, the product contains dibenzyl and benzaldehyde, in addition to unchanged toluene. In a similar manner, dimethyldibenzyl,  $\text{CHMePh}\cdot\text{CHMePh}$ , and phenylacetaldehyde were obtained from ethylbenzene.

C. F. B.

**Tertiary Parabutyltoluene and its Derivatives.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1898, [iii], 19, 67—74).—Tertiary parabutyltoluene (Bialobrzewski, *Abstr.*, 1897, i, 514) is conveniently prepared by gradually adding fuming sulphuric acid (1000 grams) containing 25 per cent. of the anhydride to a mixture of toluene (1000 grams) and isobutylic alcohol (250 grams) kept constantly stirred; its dinitro-derivative melts at 87—88° [Bialobrzewski (*loc. cit.*) gives 94—95°]. When treated with bromine (1 mol.) at 115°, it gives rise to *tertiary parabutylbenzylic bromide*,  $\text{CMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$ , which strongly irritates the eyes, and is decomposed when distilled; that the bromine atom occupies the position indicated, and has not entered the butyl radicle, appears probable from the fact that neither isobutylbenzene nor di-isobutylbenzene are attacked by bromine. *Tertiary parabutylbenzylic alcohol*,  $\text{CMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ , prepared from the bromide, boils at 140° under 20 mm. pressure, and has a sp. gr. 0.9282 at 21°; when left in contact for several hours at 60—80° with a mixture of sulphuric acid and fuming nitric acid, it gives rise to *tertiary parabutyl dinitrobenzoic acid*, which crystallises from alcohol and, when heated, sublimes without melting. *Tertiary parabutylbenzylic acetate*,  $\text{CMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OAc}$ , has an agreeable odour, boils at 137° under 20 mm. pressure, has a sp. gr. 0.9615 at 0°, and gives rise to the 2:5-dinitro-derivative,  $\text{C}_{13}\text{H}_6\text{N}_2\text{O}_6$ , which separates from alcohol in straw-coloured crystals and melts at 92.5°. *Tertiary parabutylbenzaldehyde*,  $\text{CMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , boils at 125° under 25 mm. pressure, has a sp. gr. of 0.986 at 0°, smells of bitter almonds, and, in contact with the air, is rapidly oxidised to the *acid*,  $\text{CMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , which melts at 164°; this, when treated with a warm mixture of nitric and sulphuric acids, gives rise to the dinitro-derivative just

described, but is oxidised by boiling dilute nitric acid to terephthalic acid, thus proving that all these compounds are para-derivatives.

When fuming sulphuric acid is added to a mixture of benzene and isobutylic alcohol, it gives rise to tertiary butylbenzene, but there is also formed a considerable quantity of *tertiary dibutylbenzene*,  $\text{CMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}_3$ , which forms massive crystals, melts at  $71^\circ$ , and boils at  $116\text{--}117^\circ$  under 20 mm. pressure; it does not react with the usual oxidising agents or chromyl chloride, but yields a *dinitro-derivative*, which melts at  $177^\circ$ . *Tertiary butylparacetylbenzene*, prepared by gradually adding acetic chloride (140 grams) to a mixture of tertiary butylbenzene (400 grams) and aluminium chloride (140 grams) at  $0^\circ$ , boils at  $136\text{--}138^\circ$ , has a sp. gr. of 0.9705, a refractive index  $\mu_D$  1.518 at  $15^\circ$ , and, on oxidation with dilute nitric acid, gives rise to tertiary parabutylbenzoic acid; it yields no well defined nitro-derivative, but on treating it with bromine and oxidising the product with potassium permanganate, *parisobutylphenylglyoxylic acid* is obtained.

W. A. D.

NOTE.—In the original paper, many of the compounds are spoken of as isobutyl derivatives, although the formulæ given show that tertiary butyl derivatives are meant.

W. A. D.

**Action of Amines on the Bromonitrobenzenes.** By NICOLAI N. NAGORNOFF (*Chem. Centr.*, 1898, i, 886—887; from *J. russ. chem. Ges.*, 29, 699—705).—When bromonitrobenzene is heated with an amine at  $183^\circ$ , derivatives of nitraniline are formed; dipropylparanitraniline separates in light-green crystals, melts at  $59^\circ$ , is easily soluble in alcohol, benzene, and acids, and very slightly so in water. In order to determine the effect of the position of the bromine atom, the isomeric bromonitrobenzenes were heated with diethylamine, dipropylamine, and diamylamine at  $183^\circ$  for 45 minutes. In each case, there was no reaction with metabromonitrobenzene, and the ortho- was more easily attacked than the para-derivative; with bromine, the ortho-position relatively to the nitro-group is thus the most easily replaceable. By heating orthobromonitrobenzene with triethylamine, the ammonium compound,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NEt}_3 \cdot \text{Br}$ , was obtained, the yield corresponding with 31.6 per cent. of bromine.

E. W. W.

**Electrolytic Formation of Nitrobenzene from Orthonitrobenzoic Acid.** By CARL SCHALL and R. KLEIN (*Zeit. Elektrochem.*, 1898, 5, 256—259).—In the fused state, benzoic, salicylic, orthobromoparanitrobenzoic, symmetrical dinitrobenzoic, phenylacetic, cinnamic, trichloroacetic, pyruvic, malonic, and maleic acids dissolve sodium and potassium carbonates, carbonic anhydride being evolved. Copper benzoate is soluble in fused benzoic acid. These solutions are conductors of electricity, but usually decompose more or less rapidly. Orthonitrobenzoic acid (27.9 grams) takes up 1.3 grams of anhydrous sodium carbonate, and the solution is not decomposed at  $200^\circ$ . With platinum electrodes (12 and 16 square cm. surface and 4.5 mm. apart), 0.8 to 1 ampère and about 29 volts, the formation of nitrobenzene and carbonic anhydride at the anode was observed; the

liquid becomes dark coloured, and carbonaceous masses are also formed, probably owing to reduction of the nitro-acid at the cathode.  
T. E.

**Action of Acetic Chloride on Phenyllic Acetate in Presence of Aluminium Chloride.** Preparation of Paracetophenyllic Acetate. By ALBERT VERLEY (*Bull. Soc. Chim.*, 1898, [iii], 19, 140).—When acetic chloride (1 mol.) is added, drop by drop, to a mixture of phenyllic acetate (3 mols.) with aluminium chloride (1 mol.) under diminished pressure, and the product subsequently distilled, a substance is obtained which boils at  $160^{\circ}$  under 22 mm. pressure, and forms brilliant, white crystals melting at  $54^{\circ}$ . This compound is evidently paracetophenyllic acetate, since it is oxidised by boiling with dilute nitric acid to parahydroxyacetobenzoic acid melting at  $185^{\circ}$ , and yields, on hydrolysis, parahydroxyacetophenone melting at  $110^{\circ}$ .  
N. L.

**Orthonitrobenzyllic Chloride and Paranitrobenzyllic Chloride.** By JOHANNES THIELE and OTTO DIMROTH (*Annalen*, 1899, 305, 102—123).—*Orthonitrobenzyllic methyl ether*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OMe}$ , prepared by reducing orthonitrobenzyllic chloride in methyl alcohol with sodium, is a yellow, viscous oil having a faint odour of nitrobenzene; it boils at  $130$ — $132^{\circ}$  under 15 mm. pressure, and has a sp. gr. of 1.2049 at  $15^{\circ}/4^{\circ}$ . The *ethyl ether* boils at  $167$ — $172^{\circ}$  under 50 mm. pressure.

*Orthamidobenzyllic methyl ether*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OMe}$ , cannot be prepared by the action of acidic reducing agents on the nitro-compound, and is best obtained by means of caustic soda and ferrous sulphate; it is a colourless oil which rapidly becomes brown when exposed to air, and gives the reaction for aniline with bleaching powder. The ether boils at  $123$ — $124^{\circ}$  under 30 mm. pressure, and has a sp. gr. of 1.0499 at  $17^{\circ}/4^{\circ}$ ; the *oxalate* melts at  $124^{\circ}$ . The *ethyl ether* boils at  $123$ — $129^{\circ}$  under 25 mm. pressure; the *hydrochloride* and *oxalate* melt at  $82$ — $83^{\circ}$  and  $136^{\circ}$  respectively.

*Orthohydroxybenzyllic methyl ether*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OMe}$ , is a limpid oil having the odour of guaiacol, and boils at  $128$ — $130^{\circ}$  under 40 mm. pressure; when distilled under atmospheric pressure, it becomes completely converted into resin, and as it has not the odour of coffee, it differs considerably from the caffeo of Bernheimer, which he regarded as the methyl ether of saligenin. The *ethyl ether* boils at  $111$ — $113^{\circ}$  under 20 mm. pressure, and has the odour of cresol.

*Phenyllic orthonitrobenzyllic ether*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OPh}$ , prepared from orthonitrobenzyllic chloride, phenol, and alcoholic potash, crystallises from alcohol in slender, lustrous prisms and melts at  $63^{\circ}$ .

*Phenyllic orthamidobenzyllic ether*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OPh}$ , crystallises from alcohol and melts at  $81$ — $82^{\circ}$ .

*Orthamidophenyllic orthamidobenzyllic ether*,  
 $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ ,  
 obtained by reducing orthonitrophenyllic orthonitrobenzyllic ether (Lellmann and Mayer, *Abstr.*, 1893, i, 198), crystallises from alcohol in white prisms and melts at  $118^{\circ}$ .

When paranitrobenzyllic chloride is reduced with stannous chloride,

and the alkaline liquid saturated with hydrogen sulphide, paradiamidobenzyl sulphide is produced; further reduction with zinc dust gives rise to paratoluidine. If the reduced liquid is made alkaline, and oxidised with ammonium persulphate, the *stanno*-compound,  $C_7H_9NSnO_2$ , is formed; it is insoluble in ether, alcohol, and chloroform, but dissolves readily in aniline, phenol, and glacial acetic acid.

*Diamidodibenzyl bisulphide*,  $C_{14}H_{16}N_2S_2$ , prepared by the action of hydrogen sulphide on paradiamidobenzyl alcohol (compare O. Fischer and G. Fischer, *Abstr.*, 1895, i, 343), melts at  $96-98^\circ$ ; the *hydrochloride* crystallises in slender needles, and the *acetyl* derivative melts at  $173-174^\circ$ . When paradiamidobenzyl alcohol is reduced with stannous chloride, paratoluidine is formed.

Orthonitrobenzyl chloride, when reduced with stannous chloride and treated with hydrogen sulphide, yields orthodiamidobenzyl sulphide (compare Gabriel and Posner, *Abstr.*, 1895, i, 190).

M. O. F.

**Absorption of Oxygen by Potassium Pyrogallol.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 15, 294-320).—An account of work already published. (Compare *Abstr.*, 1899, i, 645; ii, 534.) G. T. M.

**Aromatic Allylic and Propenylic Ethers.** By CHARLES MOUREU (*Ann. Chim. Phys.*, 1898 [vii], 15, 115-144).—This work has already been published. (Compare *Abstr.*, 1896, i, 215, 477, 646; 1897, i, 336, 403; 1898, i, 411, 518, 644, 660; this vol., i, 30, 125, 138.) G. T. M.

**Derivatives of Guaiacol.** By STEFANO DI BOSCOGRANDE (*Reul. Accad. Linc.*, 1897, ii, 33-35, 306-307).—*Bromethoxyguaiacol*,  $OMe \cdot C_6H_4 \cdot O \cdot C_2H_4Br$ , obtained by heating a solution of guaiacol in alcoholic potash with an excess of ethylenic bromide, crystallises in long, colourless needles melting at  $49^\circ$ , and soluble in ordinary organic solvents. *Bromethoxytrinitroguaiacol*,  $OMe \cdot C_6H(NO_2)_3 \cdot O \cdot C_2H_4Br$ , formed by the action of cold nitric acid on the preceding compound, crystallises from boiling alcohol in very minute, yellow needles melting at  $120^\circ$ . *Diguaiacylic ethylenic ether*,  $C_2H_4(O \cdot C_6H_4 \cdot OMe)_2$ , obtained by the action of bromethoxyguaiacol on guaiacol, or by treating the latter with a moderate quantity of ethylenic bromide, crystallises from boiling alcohol in large, lustrous, white needles melting at  $130^\circ$ . *Phenylic guaiacylic ethylenic ether*,  $OMe \cdot C_6H_4 \cdot O \cdot C_2H_4 \cdot OPh$ , from bromethoxyguaiacol and potassium phenoxide, crystallises in beautiful, silky needles melting at  $75^\circ$ . *Triguaiacylic phosphate*,  $PO(O \cdot C_6H_4 \cdot OMe)_3$ , obtained by the action of phosphorus pentachloride on guaiacol in benzene solution, crystallises in white prisms melting at  $91^\circ$ .

*Guaiacol picrate*,  $OH \cdot C_6H_4 \cdot OMe, C_6H_3N_3O_7$ , crystallises in minute, orange-red needles melting at  $80^\circ$  and very soluble in water and the ordinary solvents; it slowly decomposes on exposure to diffused light, the colour changing from red to yellow, whilst the melting point is raised. Picric acid is precipitated when light petroleum is added to the benzene solution of the picrate. *Benzyl-*

*guaiacol*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{OMe}$ , obtained by the action of benzylic chloride on *guaiacol* in the presence of metallic zinc, is a fluorescent, pale yellow liquid boiling at  $269\text{--}270^\circ$  under a pressure of 436 mm. and having a sp. gr. of 1.138 at  $13^\circ$ . N. L.

**Action of Mercuric Salts on Aromatic Compounds.** By OTTO DIMBOTH (*Ber.*, 1899, 32, 758—765. Compare this vol., i, 54).—All mercuric salts, such as the acetate, sulphate, and nitrate, which are decomposed by excess of water, are capable of acting on aromatic compounds, but the chloride only acts slightly even in presence of sodium acetate, and the cyanide does not act at all. The separation of thiophen from benzene, which was partially effected by Volhard (*Abstr.*, 1892, 828) by means of mercuric chloride and sodium acetate, is readily brought about by means of mercuric sulphate (Denigès, *Abstr.*, 1895, i, 411), nitrate, or acetate; in the latter case, the chief product is *thiophen dimercuric hydroxyacetate*,  $\text{OH}\cdot\text{Hg}\cdot\text{C}_4\text{H}_2\text{S}\cdot\text{Hg}\cdot\text{OAc}$ , which separates as a crystalline powder, and decomposes without melting at  $270^\circ$ ; when dissolved in acetic acid, slender needles of the *diacetate* are slowly deposited; sulphuric acid and isatin give an intense indophenin reaction with the hydroxyacetate, and hydrochloric acid decomposes it into thiophen and mercuric chloride.

Benzene is only slightly attacked by aqueous mercuric acetate at  $80^\circ$ , but at  $110\text{--}120^\circ$  it gives phenylmercuric acetate (this vol., i, 54) together with *phenylene dimercuric diacetate*,  $\text{C}_6\text{H}_4(\text{Hg}\cdot\text{OAc})_2$ , which is insoluble in benzene, separates as a powder from acetic acid, and melts at about  $230^\circ$ . Mercuric sulphate and nitrate behave similarly, but mercuric chloride is only slightly acted on by benzene even in presence of sodium acetate.

With mercuric acetate, toluene gives a mixture of salts from which sodium chloride precipitates orthotolylmercuric chloride,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{HgCl}$ , melting at  $140\text{--}142^\circ$  (Michaelis and Genzken, *Abstr.*, 1888, 146) and paratolylmercuric chloride melting at  $230\text{--}231^\circ$  (Otto, *J. pr. Chem.*, 1865, 1, 185); these were separated by fractional crystallisation, and their identity was further proved by conversion into bromotoluene.

When acted on by an excess of phenol, mercuric sulphate, nitrate and acetate are no longer precipitated by sodium hydroxide, but from an acid solution, hydroxyphenylmercuric salts are slowly deposited; mercuric chloride is only slightly attacked, but a mixture of chlorides is precipitated by sodium chloride from the product of the action of the sulphate, nitrate, and acetate. *Orthohydroxyphenylmercuric chloride*,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{HgCl}$ , is soluble in cold alcohol and melts at  $152.5^\circ$ , whilst the *benzoate* crystallises from alcohol in slender needles and melts at  $204^\circ$ . *Parahydroxyphenylmercuric chloride* is soluble in boiling alcohol, crystallises from acetone in glistening flakes, and melts at  $224\text{--}225^\circ$ ; the *benzoate* crystallises from ethylic benzoate in glistening flakes and melts at  $275\text{--}276^\circ$ . *Hydroxyphenyldimercuric dichloride*,  $\text{HO}\cdot\text{C}_6\text{H}_3(\text{HgCl})_2$ , is almost insoluble in all solvents, and melts at  $258^\circ$ ; the *benzoate* is an insoluble white powder. The substance described by Grützner (this vol., i, 198) as parahydroxyphenylmercuric chloride is a mixture of the three chlorides just described.

By the action of methylic iodide, the corresponding anisylmercuric iodides are produced. The action of ethylic iodide on orthohydroxyphenylmercuric chloride gives orthophenetylmercuric iodide and *ortho-mercuric diphenetyl*,  $\text{Hg}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$ ; this crystallises from alcohol in needles and melts at  $83^\circ$ ; it differs from the substance melting at  $224^\circ$  which was described by Michaelis (Abstr., 1894, i, 191), but its constitution is proved by the formation of orthophenetylmercuric chloride (m. p.  $132^\circ$ ) by the action of alcoholic mercuric chloride, of the acetate (m. p.  $150^\circ$ ) by the action of glacial acetic acid, and of phenetol and mercuric chloride by the action of hydrochloric acid. From an alkaline solution of orthohydroxyphenylmercuric chloride,

carbonic anhydride precipitates *orthophenylmercuric oxide*,  $\text{C}_6\text{H}_4\text{<}\overset{\text{O}}{\text{Hg}}$ , as a white powder, which is only slightly soluble in most organic solvents, but dissolves readily in phenol, in which it has a normal molecular weight according to the cryoscopic method. This substance is analogous to the orthotrimethylphenol ammonium,  $\text{C}_6\text{H}_4\text{<}\overset{\text{O}}{\text{NMe}_3}$ , described by Griess (Abstr., 1880, 636, 637); parahydroxyphenylmercuric chloride and hydroxyphenylenedimercuric dichloride give similar precipitates, but these were not obtained free from chlorine.

Catechol and quinol are oxidised by mercuric salts, but resorcinol and phloroglucinol give mercuric compounds, as also do the phenylic ethers, benzoic and salicylic acids, naphthalene and the naphthols, phenanthrene, anthracene, and aromatic amines (Pesci, Abstr., 1898, i, 648).

T. M. L.

**Action of Titanium Chloride on Organic Compounds.** By ANDRÉ KLING (*Bull. Soc. Chim.*, 1898, 19, [iii], 190).—Aniline, free from toluidine, when dissolved in chloroform or benzene and treated in the cold with titanium chloride, yields a colouring matter of the rosaniline type which leaves a notable amount of titanium oxide on ignition. When the experiment is performed at high temperatures in the absence of solvents, a colouring matter of the violaniline series is produced. It is suggested that the former product is a rosaniline containing an atom of titanium, replacing the methane carbon atom of pararosaniline, and that the compound is decomposed by heat into the violaniline derivative. When anisole is treated in a similar manner, it yields methylic chloride and phenylic orthotitanate.

G. T. M.

**Reactions of Mercurio-aniline.** By G. MONTECCHI (*Gazzetta*, 1898, 28, ii, 434—436).—Thiourea and mercurio-aniline, when ground together in molecular proportion, readily react with the separation of mercuric sulphide and formation of dicyanodiamide.

When diphenylthiourea and mercurio-aniline, in molecular proportion, are intimately mixed in presence of a small quantity of aqueous aniline, a rise of temperature occurs, accompanied by the production of a black, pasty mass, which, on extraction with boiling alcohol, yields triphenylguanidine.

T. H. P.

**Compounds of Mercury with Organic Bases.** By LEONE PESCI (*Gazzetta*, 1898, 28, ii, 436—477).—The author gives a summary of the results obtained by himself and his pupils in their work on this subject during the period 1892—1898 (see Abstr., 1890, 1211; 1891, 268; 1892, 1448; 1893, i, 24, 304, 322; 1894, i, 248, 249; 1895, i, 357, 358; 1896, i, 186, 388; 1897, i, 36, 328, 337, 370, 559; this vol., i, 361, and preceding abstract). T. H. P.

**Reaction of Orthodiazobenzoic Acid with Sulphurous Acid and Copper Powder.** By WILLIAM E. HENDERSON (*Amer. Chem. J.*, 1899, 21, 206—210).—When a solution of orthodiazobenzoic acid sulphate is added to a cold saturated solution of sulphurous anhydride in which copper powder is suspended, nitrogen is evolved. A considerable amount of copper passes into solution, part of the sulphurous acid is oxidised to sulphuric, and, instead of orthosulphobenzoic acid, the chief product is dithiosalicylic acid (List and Stein, Abstr., 1898, i, 697), the yield being about 50 per cent. of the theoretical. J. J. S.

**Salts of Benzyldenehydrazinesulphonic Acid.** By ROBERT STOLLE (*Ber.*, 1899, 32, 799—800).—If the product obtained by the interaction of anhydrous hydrazine with potassium pyrosulphate is neutralised with aqueous potassium carbonate, extracted with benzaldehyde, filtered, dried in a vacuum and extracted with a large quantity of hot alcohol, *potassium benzyldenehydrazinesulphonate*,  $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{SO}_3\text{K}$ , crystallises from the solution on cooling; it forms glistening leaflets, readily taking up water and forming benzaldehyde and potassium hydrazinesulphonate. It reduces ammoniacal silver solution on warming, and is completely decomposed by mineral acids into benzaldehyde, hydrazine, and sulphuric acid. On the addition of barium chloride, its solution becomes coloured an intense yellow and gradually deposits a rose coloured powder probably having the constitution  $(\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{SO}_3\cdot\text{Ba})_2\text{O}$ .

Potassium hydrazinesulphonate reduces ammoniacal silver nitrate in the cold. J. F. T.

**Acetanilide and Hypochlorites.** By NICOLA CASTORO (*Gazzetta*, 1898, 28, ii, 312—316).—By the action of bleaching powder on a solution of acetanilide acidified with acetic acid, Bender (Abstr., 1887, 44) obtained the compound,  $\text{Ph}\cdot\text{NClAc}$ , melting at  $91^\circ$ . The author has been unable to isolate this substance, but finds that the reaction of the two substances mentioned always gives rise to parachloroacetanilide and 1:4-dichloroacetanilide in proportions depending on the relative quantities of acetanilide, hypochlorite, and acetic acid employed.

T. H. P.

[NOTE.—Bender's statement is correct, and the compound has been obtained frequently in the laboratory of the Central Technical College, London.—EDITOR].

**Action of Sulphuric Acid on Symmetrical Aromatic Carbamides.** By PAUL CAZENEUVE and MOREAU (*Bull. Soc. Chim.*, 1898, [iii], 19, 21—25).—When symmetrical diphenylcarbamide is



warmed with sulphuric acid of sp. gr. 1.711 at a temperature not exceeding  $110^{\circ}$ , it gives rise to the compound,  $\text{COOH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ , which is decomposed, on further heating, into carbonic anhydride and sulphanilic acid. Symmetrical diparatolylcarbamide does not yield the intermediate carboxylic compound, but at  $150\text{--}160^{\circ}$  gives rise to a mixture of paratoluidine-ortho- and -meta-sulphonic acids. Symmetrical diorthotolylcarbamide, under similar treatment, yields orthotoluidine-3-sulphonic acid, whilst dimetaxylylcarbamide gives a product apparently identical with 4-metaxylylidine-6-sulphonic acid (Jacobsen and Ledderboge, *Abstr.*, 1883, 593). Di- $\psi$ -cumylcarbamide (*Abstr.*, 1897, i, 519) gives rise to no definite product, whilst dixylylcarbamide [ $\text{Me}_2:\text{NH}=1:2:4$ ] yields a new 4-*orthoxylylidine-sulphonic acid*, which probably contains the sulpho-group in position 6. The action of sulphuric acid on the symmetrical carbamides derived from 3-orthoxylylidine and 2-paraxylylidine is being studied.

W. A. D.

**Rearrangement of Imido-ethers.** By HENRY L. WHEELER and T. B. JOHNSON (*Amer. Chem. J.*, 1899, 21, 185—193).—It is suggested that formethylanilide is produced from phenyl formimidoethylic ether (this vol., i, 354) by the addition and subsequent loss of ethylic iodide, a view which finds support from the fact that benzimidoethylic ether,  $\text{OEt}\cdot\text{CPh}\cdot\text{NH}$ , when heated at  $100^{\circ}$  with ethylic iodide, yields ethylbenzamide,  $\text{COPh}\cdot\text{NH}\cdot\text{Et}$ . This reaction was studied quantitatively, and, in addition to ethylbenzamide, benzamide, benzonitrile, and cyaphenin were isolated in relatively small amounts. These are the first cases observed in which a silver salt of an acyclic amide, anilide, or imido-ether gives alkylic derivatives of this type with alkylic iodides. Formethylanilide boils at  $259\text{--}266^{\circ}$  under 772 mm. pressure, the boiling point being  $258^{\circ}$  under 728 mm. pressure, according to Pictet and Crépieux (*Abstr.*, 1888, 688). Ethylbenzamide boils at  $298\text{--}299^{\circ}$ , and not at  $256\text{--}260^{\circ}$ , as Schmidt and Gattermann state (*Abstr.*, 1887, 358).

J. J. S.

**Azonium Chromogenes.** By W. SCHAPOSCHNIKOFF (*Chem. Centr.*, 1898, i, 722—723; from *J. russ. chem. Ges.*, 29, 535—565. Compare *Abstr.*, 1897, i, 172, 491).—The author arrives at the following conclusions: (1) Aposafraanine and induline are amido-derivatives of azonium bases, and can be converted into these bases by diazotising, &c.; (2) the azonium bases are strong bases, and even form carbonates; (3) the behaviour and properties of the azonium bases are very similar to those of the acetyl derivatives of aposafraanine and rosinduline; (4) the azonium bases give substitution reactions which have hitherto been considered characteristic of the orthoquinones; (5) phenylphenazonium and phenylnaphthazonium are the chromogenes of the safranines and the indulines.

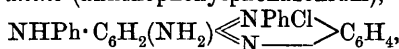
Acetylposafraanine carbonate, obtained by passing dry carbonic anhydride into the ethereal solution of the base, forms brown crystals, and is decomposed by water. Phenylphenazonium is best isolated as the double salt with ferric chloride; the dichromate,  $(\text{C}_{18}\text{H}_{13}\text{N}_2)_2\text{Cr}_2\text{O}_7$ ,

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forms a dark violet precipitate, or crystallises from water in yellow prisms; the platinumchloride,  $C_{18}H_{13}N_2PtCl_6$ , is an almost insoluble microcrystalline powder; the aurichloride,  $C_{18}H_{13}N_2AuCl_4$ , is a yellow powder; the mercurichloride,  $C_{18}H_{13}N_2HgCl_2$ , forms an orange-yellow precipitate, and is very slightly soluble in water, and the picrate a brownish-red precipitate which crystallises from water in slender needles. A good yield of aposafranone,  $C_6H_3O \llcorner \begin{smallmatrix} N \\ \text{NPh} \end{smallmatrix} \gg C_6H_4$ , is obtained by decomposing the ferric chloride compound of phenylphenazonium with a dilute solution of sodium hydroxide in alcohol, filtering the ferric hydroxide, acidifying, passing air through the warm solution, precipitating with sodium acetate, and finally crystallising from benzene.

*Dimethylaposafranine*,  $NMe_2 \cdot C_6H_3 \llcorner \begin{smallmatrix} N \\ \text{NPhCl} \end{smallmatrix} \gg C_6H_4$ , prepared by the action of dimethylamine on the ferric chloride compound of phenylphenazonium dissolved in alcohol, air being passed through the mixture, crystallises from water in thick prisms, and gives a violet solution in alcohol which is not fluorescent; the platinumchloride and chromate are very slightly soluble microcrystalline powders.

*Phenylaposafranine* (anilinophenylphenazonium),



is obtained by the action of aniline on an alcoholic solution of the ferric chloride compound of phenazonium, air being passed through the mixture. The hydrochloride crystallises in dark blue prisms, and dyes wool and silk heliotrope.

*Anilinophenylaposafranine*,  $C_6H_2(NHPh)_2 \llcorner \begin{smallmatrix} NPhCl \\ N \end{smallmatrix} \gg C_6H_4$ , prepared by the action of 7 parts of aniline on 1 part of phenazonium, separates in dark green crystals, gives a red solution in alcohol, but is insoluble in water.

*Dimethylrosinduline*,  $C_6H_4 \cdot C_6H(NMe_2) \llcorner \begin{smallmatrix} N \\ N(NO_3)Ph \end{smallmatrix} \gg C_6H_4$ , prepared from phenylnaphthaphenazonium in the same way as the corresponding safranine is obtained from the corresponding phenazonium, crystallises in green leaflets from water containing a little acid, and dyes wool and silk carmin red; the reddish-violet platinumchloride and the dark red chromate are very slightly soluble. Rosindone is prepared in a similar manner to aposafranine. Naphthaphenosafraanine, prepared by the action of ammonia on acetylmonamidophenylnaphthaphenazonium, resembles phenosafranine in its behaviour and the properties of its salts and derivatives; it separates in dark green crystals and is easily soluble in water, forming a cherry-red solution with orange-yellow fluorescence. By methods of preparation similar to that of naphthaphenosafraanine, the following compounds may be obtained: anilinonaphthaphenosafraanine, which dyes silk bluish-green; a piperidine derivative which dyes wool and silk rose, resembling in shade that of Magdala red, and a metatoluylenediamine derivative, which dyes wool and silk mauve.

E. W. W.

**Nitracetophenone and Nitracetone.** By AD. LUCAS (*Ber.*, 1899, 32, 600—607. For other nitroketones compare Hollemann, *Abstr.*, 1897, i, 599; and also *Trans.*, 1898, 73, 991, and 1899, 75, 211).—*α*-Iodacetophenone,  $\text{COPh}\cdot\text{CH}_2\text{I}$ , melts at  $28^\circ$ , and has an irritating odour similar to that of the bromo-compound; in ethereal solution, it gradually decomposes, with liberation of iodine. *α*-Isonitracetone is produced, together with a substance melting at  $205^\circ$ , by the action of silver nitrite on *α*-iodacetophenone; it crystallises from ether and melts at  $108^\circ$ . It is easily soluble in ether, alcohol, and benzene, slightly soluble in cold water, and on cooling separates in fine needles from an aqueous solution saturated at  $30^\circ$ ; the aqueous solution, however, decomposes slowly in the cold, and rapidly if heated above  $30^\circ$ ; the alcoholic solution decomposes yet more rapidly, with formation of ethylic benzoate and nitrous acid; the solid is stable in dry air. The aqueous solution is acid to litmus, and gives a faint colour with ferric chloride, which gradually deepens to an intense reddish-brown; the same colour appears immediately in ethereal solution. The substance is soluble in caustic soda and in sodium carbonate, giving a neutral sodium salt, from which it is precipitated again unchanged by the addition of acids. The ammonium salt is precipitated by dry ammonia from a solution of the substance in dry ether or benzene, but phosphorus pentachloride and acetic chloride have no action on an anhydrous solution. The salts give an immediate coloration with ferric chloride, which disappears more rapidly than is the case with the free acid, owing to decomposition into a benzoate and nitrous acid; a similar decomposition is effected immediately by concentrated sulphuric acid.

*Ammonium-isonitracetone* is a white salt which decomposes in the desiccator, becoming orange-red in colour, and giving off a strong odour of mice; the orange-yellow solution gives a deep red-brown coloration with ferric chloride, which does not appear again, as the products of decomposition are nitrous acid and red ferric acetate. *Nitracetone* was obtained as a yellow oil\* smelling slightly of acetic acid; its aqueous solution is acid, and gives an immediate reddish-brown coloration with ferric chloride, but only gradually acts on a solution of starch and potassium iodide. With hydroxylamine, nitracetone forms a salt, but not an oxime, and nitracetophenone behaves in the same way. The colourless liquid, boiling at  $152^\circ$ , which was prepared by L. Henry and de Battice (*Bull. Acad. Roy. Belg.*, [iii], 36, 149) by the oxidation of nitroisopropyl alcohol, and described by them as nitroacetone, is regarded by the author as an entirely different substance.

T. M. L.

**Orthohydroxyphenoxyacetone.** By CHARLES MOUREU (*Compt. rend.*, 1899, 128, 433—435. Compare this vol., i, 125).—*Orthohydroxyphenoxyacetone*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COMe}$ , obtained by the action of chloracetone on monosodiumcatechol, forms brilliant white, long, slender needles which melt at  $98$ — $99^\circ$  and dissolve in alcohol, ether, or boiling water, but are only slightly soluble in cold water. It boils at  $169$ — $170^\circ$  under 46 mm. pressure, and is only slightly volatile in

\* This is probably a mixture of nitracetone and isonitracetone in equilibrium, similar to those produced by fusing other nitroketones.—T. M. L.

steam, gives no reaction with ferric chloride, but reduces ammoniacal silver nitrate. The acetate,  $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COMe}$ , boils at  $176-180^\circ$  under 19 mm. pressure; the phenylhydrazone melts at  $113^\circ$ , and the oxime, which crystallises in small prisms, at  $76-77^\circ$ .

By interaction with a mixture of alcohol and ethylic imidoformate hydrochloride (which produces ethylic orthoformate), the orthohydroxyphenoxyacetone yields the acetal,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CMe}(\text{OEt})_2$ , and this, when heated, splits up into alcohol and ethoxymethylethane-

catechol,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CMe} \cdot \text{OEt} \end{smallmatrix}$ , a colourless, odourless, neutral, oily liquid, which boils at  $124-125^\circ$  under 15 mm., and at  $233-237^\circ$ , with partial decomposition, under ordinary pressure, is volatile in steam and has a sp. gr. of 1.1271 at  $0^\circ$ . When boiled with dilute sulphuric acid, it yields alcohol and orthohydroxyphenoxyacetone. C. H. B.

**Aromatic Ketones containing Iodine.** By A. COLLET (*Compt. rend.*, 1899, 128, 312—313).—*Phenyl iodomethyl ketone*,  $\text{CH}_2\text{I} \cdot \text{COPh}$ , prepared by warming an alcoholic solution of phenyl chloromethyl ketone at  $45-50^\circ$  for 2 hours with finely powdered potassium iodide, crystallises from alcohol in colourless needles, and melts at  $29.5-30^\circ$ ; on oxidation with hot alkaline potassium permanganate, it yields benzoic acid, whilst when warmed with lead hydroxide suspended in water, it forms benzoylcarbinol.

*Paratolyl iodomethyl ketone*,  $\text{C}_7\text{H}_7 \cdot \text{CO} \cdot \text{CH}_2\text{I}$ , prepared from paratolyl chloromethyl ketone, forms colourless needles, melts at  $40-41^\circ$ , and on oxidation yields terephthalic acid; alcoholic potassium acetate converts it into paratoluoylcarbinyl acetate, which melts at  $83^\circ$ .

*Paratolyl iodethyl ketone*,  $\text{C}_7\text{H}_7 \cdot \text{CO} \cdot \text{CHMeI}$ , crystallises from alcohol in colourless, lustrous plates, melts at  $102-103^\circ$ , and on oxidation with warm alkaline potassium permanganate yields paratoluic and terephthalic acids; alcoholic potassium acetate converts it into methylparatoluoylcarbinyl acetate,  $\text{C}_7\text{H}_7 \cdot \text{CO} \cdot \text{CHMe} \cdot \text{OAc}$ , which melts at  $106^\circ$ .

These ketones are acted on by light, iodine being liberated, and their vapours strongly irritate the eyes. W. A. D.

**Application of Friedel and Craft's Method of Synthesis in the Preparation of Aromatic Aldehydes and Ketones under Reduced Pressure.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1898, [iii], 19, 137—140. Compare this vol., i, 207).—In reply to Bouveault (*Bull. Soc. Chim.*, [iii], 17, 1020), the author contends that, although some loss undoubtedly occurs when operating under reduced pressure with volatile compounds, like acetic chloride, or with such as dissociate, like ethylic cymylglyoxalate, yet the method described by him is, as a rule, attended with considerable advantages. In the preparation of *isobutyrylparacymene*, a liquid of sp. gr. 0.957 at  $0^\circ$ , and boiling at  $152^\circ$  under 20 mm. pressure, or at  $260-262^\circ$  under atmospheric pressure, the yield is 97 per cent., and an almost theoretical yield is also obtained in the case of *acetothymylic methylic ether*, which boils at  $155^\circ$  under 20 mm. pressure. The boiling point of ethylic cymylglyoxalate is  $186^\circ$  under 21 mm. pressure, and not  $130-132^\circ$  as

was previously stated through a clerical error. With regard to the objections raised against the use of bromine, the author finds that substitution always takes place in the side chain of ketones, and not in the aromatic nucleus. Should the latter case occur, however, the difficulty would be obviated by the use of chloracetic chloride instead of acetic chloride. N. L.

**Formation of Ketones with the aid of Aluminium Chloride.** By J. BOESEKEN (*Bull. Soc. Chim.*, 1898, [iii], 19, 349—350).—In the preparation of ketones by the interaction of aromatic hydrocarbons with aliphatic acid chlorides, almost theoretical yields are obtained if care is taken that the aluminium chloride, freshly prepared, is always in excess, and that the reaction does not extend over too long a time. The temperature may conveniently be that of boiling carbon bisulphide, at which hydrogen chloride is regularly evolved, and operating under reduced pressure, as proposed by Verley (preceding abstract) is unnecessary. The large yields obtained by the latter method are attributed to the fact that the arrangement of the apparatus for working in a vacuum necessitates the presence of an excess of aluminium chloride during the greater part of the reaction. By the gradual addition of a mixture of phenetol (50 grams) with acetic chloride (50 grams) to 100 grams of aluminium chloride covered with a layer of boiling carbon bisulphide, 64·3 grams of parethoxyphenyl methyl ketone were obtained—a yield of nearly 96 per cent. of the theoretical. N. L.

**Action of Aniline on Dinitrophenyldiacetylmethane.** By FERNAND MUTTELET (*Bull. Soc. Chim.*, 1898, [iii], 19, 74).—When dinitrophenyldiacetylmethane (this vol., i, 281) is heated with aniline (1 mol.) for 8 hours at 100—105°, it gives rise to acetanilide together with *dinitrophenylacetylmethane*,  $\text{CH}_2\text{Ac}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , which crystallises from alcohol in lustrous leaflets, and melts at 73—75°. W. A. D.

**New Method of Preparing  $\alpha$ -Methylcinnamic Acid from  $\beta$ -Phenyl- $\alpha$ -methylethylenelactic Acid.** By G. DAIN (*Chem. Centr.*, 1898, i, 674—675; from *J. russ. chem. Ges.*, 29, 607—614).— $\alpha$ -Methylcinnamic acid is prepared by heating  $\beta$ -phenyl- $\alpha$ -methylethylenelactic acid (1 mol.) with acetic chloride or acetic anhydride (2 mols.) at 100—180° for 12—20 hours. The calcium salt,  $\text{Ca}(\text{C}_{10}\text{H}_9\text{O}_2)_2 + 3\text{H}_2\text{O}$ , crystallises in slender needles, is easily soluble in hot and very soluble in cold water; the silver salt,  $\text{AgC}_{10}\text{H}_9\text{O}_2$ , crystallises in feathery clusters, and the barium salt in small prisms.

The stereoisomeric acid,  $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{H} \\ | \\ \text{COOH}\cdot\text{C}\cdot\text{Me} \end{array}$ , obtained from the salts, crystallises from ether in monoclinic prisms and melts at 81—82°. When recrystallised from light petroleum, it is partially converted

into the more stable isomeride,  $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{H} \\ | \\ \text{Me}\cdot\text{C}\cdot\text{COOH} \end{array}$ , which is also

formed by distilling methylcinnamic acid, and crystallises in long, flexible needles melting at 74°. By the action of concentrated sulphuric acid at 120° for 6 hours,  $\alpha$ -methylcinnamic acid yields allylbenzene and methronene. E. W. W.

**Action of Zinc on Ethylic  $\alpha$ -Bromopropionate and Benzaldehyde (Synthesis of  $\beta$ -Phenyl- $\alpha$ -methylethylenelactic Acid).** By G. DAIN (*Chem. Centr.*, 1898, i, 668; from *J. russ. chem. Ges.*, 29, 597—607).—Ethylic  $\beta$ -phenyl- $\alpha$ -methylethylenelactate is prepared by the action of ethylic  $\alpha$ -monobromopropionate (50 grams) on benzaldehyde (31 grams) in presence of granulated zinc. The intermediate bromo-zinc compound formed in this reaction, when boiled with absolute alcohol or water, also yields the ethylic salt. The acid, obtained by hydrolysing the ethylic salt with baryta water, crystallises from light petroleum; the *sodium* salt,  $C_{10}H_{11}O_3Na + 2H_2O$ , crystallises from water; the *calcium* salt crystallises with  $4H_2O$ ; the *barium* salt,  $Ba(C_{10}H_{11}O_3)_2 + 3\frac{1}{2}H_2O$ , crystallises in needles or prisms; the *zinc* salt,  $Zn(C_{10}H_{11}O_3)_2 + H_2O$ , crystallises in needles; the *silver* salt,  $AgC_{10}H_{11}O_3$ ; the *ammonium* salt crystallises in long, slender, matted needles; the *lead* salt forms scales which become nodular after prolonged digestion with water; the *copper* salt is very soluble in ether and alcohol and soluble in water.

E. W. W.

**Action of Zinc on Ethylic Bromisovalerate and Benzaldehyde.** By G. DAIN (*Chem. Centr.*, 1898, i, 884—885; from *J. russ. chem. Ges.*, 29, 659—666).—Ethylic  $\beta$ -phenyl- $\alpha$ -isopropylethylenelactate is prepared by dropping a cooled mixture of benzaldehyde (51 grams) with ethylic bromisovalerate (105 grams) on to granulated zinc, allowing the product to remain 4 days, and then acidifying with dilute sulphuric acid; it forms a viscous liquid with an odour recalling that of pineapple. The acid, obtained by hydrolysing the ethylic salt with baryta water, crystallises in slender needles from a mixture of light petroleum and benzene, melts at  $106-107^\circ$ , is easily soluble in ether, alcohol, ethylic acetate, and acetic acid, very slightly soluble in light petroleum and benzene, and is volatilised by steam; 100 parts of water at  $18^\circ$  dissolve 4.79, and at  $100^\circ$ , 4.83 parts of acid. The *calcium* salt,  $Ca(C_{12}H_{15}O_3)_2$ , forms white crystals, the *sodium* salt,  $NaC_{12}H_{15}O_3 + 4H_2O$ , nodules, and the *barium* and *potassium* salts are very hygroscopic. The *silver* salt,  $AgC_{12}H_{15}O_3$ , is formed as a white, amorphous precipitate which dissolves in hot water, but does not separate again on cooling. Only a small portion of the acid distils unchanged at  $201-210^\circ$ , the greater part decomposing into carbonic anhydride, water, and phenylpropylethylene,  $CHPh:CHPr$ . By the action of sulphuric acid on the acid, phenylpropylethylene and small quantities of isovaleric and benzoic acids are formed; the latter acid is derived from the benzaldehyde.

E. W. W.

**Oxidation of Phenylhydroxypivalic Acid.** By G. DAIN (*Chem. Centr.*, 1898, i, 889; from *J. russ. chem. Ges.*, 29, 656—659).—When 3 grams of potassium permanganate in 2 per cent. solution are added in small portions to 5.4 grams of potassium phenylhydroxypivalate in 2 per cent. solution at the ordinary temperature, benzaldehyde and potassium isobutyrate are first formed and are then oxidised to potassium benzoate and potassium  $\alpha$ -hydroxyisobutyrate.

E. W. W.

**Hydroxyphenylglyoxylic Acids. Synthesis of Vanillin.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, [iii], 19, 75—77).—When paramethoxyphenylglyoxylic acid is heated with 30 per cent. aqueous caustic potash for 12 hours at  $170^{\circ}$ , it is converted into *parahydroxyphenylglyoxylic acid*, which, on adding benzene to the ethereal solution, separates in hard, lustrous crystals melting at  $172\text{--}173^{\circ}$ . Veratroyl-carboxylic acid, when similarly treated, is partially resolved into vanilloyl- and catechoyl-carboxylic acids; on boiling the crude product for 1 hour with dimethylaniline (compare Gassmann, *Abstr.*, 1897, i, 343), subsequently with 10 per cent. sulphuric acid, and finally extracting with ether, vanillin is obtained along with veratric aldehyde. On shaking the ethereal solution with aqueous sodium carbonate, the vanillin alone is removed, and can be obtained in a pure state by acidifying with hydrochloric acid, extracting with ether, shaking with aqueous sodium hydrogen sulphite, acidifying the solution so obtained, and finally extracting with ether. W. A. D.

**Phenylitaconic Acid and its Isomerides.** By RUDOLPH FITTIG and ARTHUR BROOKE (*Annalen*, 1899, 305, 19—41. Compare Fittig and Leoni, *Abstr.*, 1890, 894).—Phenylitaconic acid melts at  $192^{\circ}$ , evolving water vapour; it crystallises slowly from ether in elongated twinned needles belonging to the asymmetric system, [ $a:b:c=0.82:1:0.75$ ;  $\alpha=105^{\circ} 47'$ ,  $\beta=118^{\circ} 53'$ ,  $\gamma=84^{\circ} 59'$ ]. The *anhydride* crystallises from chloroform in transparent leaflets belonging to the monosymmetric system, and liquefies at  $164\text{--}166^{\circ}$ , yielding the *anhydride* of phenylcitraconic acid,  $C_{11}H_8O_3$ ; this substance melts at  $60\text{--}61^{\circ}$ , and separates from ether in monosymmetric crystals, [ $a:b:c=0.9498:1:0.5291$ ;  $\beta=80^{\circ} 53'$ ]. The anhydride of phenylitaconic acid is regenerated when the anhydride of phenylcitraconic acid is heated at  $170^{\circ}$ . *Phenylcitraconic acid*,  $CH_2Ph \cdot C(COOH) \cdot CH \cdot COOH$ , crystallises from a mixture of ether and petroleum, and melts at  $105\text{--}108^{\circ}$ , losing water; the crystals belong to the asymmetric system, [ $a:b:c=0.5830:1:0.2467$ ;  $\alpha=122^{\circ} 25'$ ,  $\beta=103^{\circ} 15'$ ,  $\gamma=56^{\circ} 10'$ ]. The *sodium*, *calcium*, and *silver* salts are anhydrous, whilst the *barium* salt contains  $1H_2O$ . When boiled with water, phenylcitraconic acid yields about 33 per cent. of phenylitaconic acid.

*Phenylmesaconic acid*,  $CH_2Ph \cdot C(COOH) \cdot CH \cdot COOH$ , separates in leaflets when a small quantity of a dilute solution of bromine in chloroform is added to phenylcitraconic acid exposed to sunlight; it crystallises from boiling water in flattened needles, and melts at  $212^{\circ}$ . The *calcium* salt contains  $2\frac{1}{2}H_2O$ , and the *barium* salt  $2H_2O$ , the *silver* salt being anhydrous.

*Phenylatronic acid*,  $C_{11}H_{10}O_4$ , prepared by the action of boiling aqueous caustic soda on phenylitaconic acid, melts at  $149\text{--}151^{\circ}$ ; the crystals from ether are monosymmetric, [ $a:b:c=1.0333:1:1.0482$ ;  $\beta=60^{\circ} 55'$ ]. The *calcium* and *barium* salts contain  $2H_2O$ , and the *silver* salt remains unchanged in weight and appearance at  $100^{\circ}$ . The *anhydride* crystallises from chloroform in needles, and melts at  $138\text{--}140^{\circ}$ ; boiling water converts it into the acid. Phenylitaconic acid is regenerated from phenylatronic acid by the action of a small

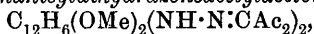
quantity of bromine under the influence of sunlight; the same effect is produced by a boiling 10 per cent. solution of caustic soda during 20 hours.

The quantitative effects of treating these four acids with a boiling solution of caustic soda are summarised in tabular form. Benzylsuccinic acid is obtained on reducing the four isomerides with sodium amalgam.

M. O. F.

**Action of the Bis-diazochlorides of Benzidine, Orthotolidine, and Orthodianisidine on Acetylacetone.** By G. FAVREL (*Compt. rend.*, 1899, 128, 318—319).—*Diphenyldihydrazoneacetylacetone*,  $C_{12}H_8(NH \cdot N : CAc_2)_2$ , prepared by adding acetylacetone to an ice cold solution of tetrazodiphenyl chloride and subsequently saturating with aqueous caustic soda, sodium carbonate, or, best, with sodium acetate, is insoluble in the usual solvents, but crystallises from nitrobenzene or aniline in beautiful, red needles and melts at 258—260°; it is insoluble in aqueous alkalis, but yields, with sodium ethoxide, a sodium derivative which is easily decomposed by water and does not react with methylic iodide or benzoic chloride. Attempts to prepare the more complex hydrazones by acting on diphenyldihydrazoneacetylacetone with phenylhydrazine were unsuccessful.

*Diorthotolyldihydrazoneacetylacetone*,  $C_{12}H_6Me_2(NH \cdot N : CAc_2)_2$ , prepared from tetrazo-orthoditoly chloride, forms red needles melting at 250—252°, and *diorthanisylldihydrazoneacetylacetone*,



crystallises similarly and melts at 234—235°.

W. A. D.

**Orthodiamidodibenzyl.** By JOHANNES THIELE and OTTO HOLZINGER (*Annalen*, 1899, 305, 96—102. Compare Thiele and Dimroth, *Abstr.*, 1895, i, 534).—Although orthodiamidostilbene, when heated with the dihydrochloride, yields dihydroindole and aniline (*loc. cit.*), the corresponding derivative of dibenzyl undergoes the normal change, yielding orthoimidodibenzyl by elimination of ammonia from two molecules.

*Orthodiamidodibenzyl*,  $C_2H_4(C_6H_4 \cdot NH_2)_2$ , prepared by reducing orthodiamidostilbene, dissolved in amyl alcohol, with sodium, crystallises from dilute alcohol in small, white needles melting at 68°. The *dihydrochloride* crystallises in colourless needles containing  $2H_2O$ , and does not melt below 270°, whilst the picrate forms yellow needles which melt and decompose at 225—230°; the *diacetyl* and *dibenzoyl* derivatives melt at 249—250° and 255° respectively.

*Orthodihydroxydibenzyl*,  $C_2H_4(C_6H_4 \cdot OH)_2$ , obtained from the foregoing base by decomposing the diazo-compound with water, crystallises from water and melts at 115°.

*Orthodichlorodibenzyl*,  $C_2H_4(C_6H_4Cl)_2$ , crystallises from alcohol in colourless, lustrous leaflets, and melts at 65°.

*Orthoimidodibenzyl*,  $C_6H_4 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{---} \text{NH} \text{---} \end{array} C_6H_4$ , produced on heating orthodiamidodibenzyl with the anhydrous hydrochloride at 265—275° during 26—30 hours, melts at 110°, and crystallises from petroleum in prisms belonging to the monoclinic system, [ $a : b : c = 1.4308 : 1 : 1.0373$ ;  $\beta = 91^\circ 52'$ ]. The substance is volatile in steam, and when dissolved



in concentrated sulphuric acid yields a deep blue coloration with a small quantity of nitric acid. The *nitroso*-derivative crystallises from ether in small, yellow needles, and melts at 120°.

M. O. F.

**Triphenylvinyllic Alcohol or Triphenylethanone.** By HEINRICH BILTZ (*Ber.*, 1899, 32, 650—658).—The substance,  $C_{20}H_{16}O$ , prepared by the author from chloral and benzene in presence of aluminium chloride (Abstr., 1893, i, 718), and by Saint-Pierre (*Bull. Soc. Chim.*, 1891, [iii], 5, 292), Klingemann (Abstr., 1893, i, 590), and Delacre (Abstr., 1896, i, 485), by other methods, may have the formula  $CPh_2:CPh\cdot OH$  or  $CHPh_2\cdot CPh$ . The author prefers the enolic formula, since the substance gives an acetyl (Biltz, Abstr., 1897, i, 533) and a benzoyl derivative, although, like triphenylcarbinol, it does not interact with phenylcarbimide. There is no evidence for the ketonic formula, since the substance does not form an oxime or a phenylhydrazone (Delacre, Biltz), and does not interact with hydrazine or aniline. The presence of a double bond is indicated by the formation of an alcoholate,  $OEt\cdot CPh_2\cdot CHPh\cdot OH$ , which, when oxidised, yields ethylphenylbenzoin. The dibromide could not be isolated, since it immediately loses hydrogen bromide, and gives the compound  $CPh_2Br\cdot CPh$ .

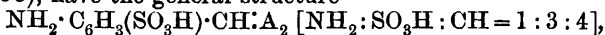
*Triphenylvinyllic benzoate*,  $CPh_2:CPh\cdot OBz$ , crystallises from alcohol in prisms, and melts at 153°; it is readily hydrolysed by alcoholic potash, but is stable towards acids.

The ketonic formula is rendered the less probable by the fact that the closely related phenylbenzoin,  $OH\cdot CPh_2\cdot CPh$ , readily yields ketonic derivatives. This substance, best prepared by the oxidation of triphenylvinyllic alcohol, crystallises from dilute alcohol or from a mixture of chloroform and petroleum, and melts at 84—85°; it is readily reduced to triphenylvinyllic alcohol by stannous chloride. *Phenylbenzoinhydrazone*,  $OH\cdot CPh_2\cdot CPh:N\cdot NH_2$ , crystallises from alcohol in colourless needles, and melts at 167—168°. *Phenylbenzoin-metanitrobenzylidenazine*,  $OH\cdot CPh_2\cdot CPh:N\cdot N:CH\cdot C_6H_4\cdot NO_2$ , prepared by the action of metanitrobenzaldehyde on the hydrazine, crystallises from alcohol in yellow, transparent needles, and melts at 123°.

The author applies Drude's method for determining the absorption of electric waves, in order to confirm the presence of the hydroxyl-group in the substance (Abstr., 1897, ii, 537), and shows that, whilst the related non-hydroxylic compounds do not absorb these waves, triphenylvinyllic alcohol and other hydroxylic compounds exhibit absorption in the liquid, but not in the solid, state; triphenylcarbinol and ethylphenylbenzoin,  $OH\cdot CPh_2\cdot CO\cdot Ph$ , are quoted as exceptions.

T. M. L.

**Malachite-green-orthosulphonic Acid.** By SUAIS (*Bull. Soc. Chim.*, 1898, [iii], 19, 25—27).—The sulpho-leuco-bases formed by the interaction of benzhydrols with metasulphanilic acid (compare this vol., i, 58), have the general structure



where A denotes a radicle of the type  $C_6H_4\cdot NR_2$ . The leuco-base

derived from tetramethyldiamidobenzhydrol (*loc. cit.*) would thus be malachite-green-orthosulphonic acid,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , probably identical with the substance obtained by Sandmeyer by acting on benzaldehydeorthosulphonic acid with dimethylaniline.

W. A. D.

**Tetrahydropyrone Compounds. II.** By PAVEL IW. PETRENKO-KRITSCHENKO (*Ber.*, 1899, 32, 809—812).—Not only does hydrochloric acid convert hydropyrones into unsaturated ketones (*Abstr.*, 1898, i, 529), but other mineral acids possess the same property, and it is only necessary to add a few drops of a mineral acid to an alcoholic solution of a hydropyrone, and boil, to bring about its complete conversion into the unsaturated ketone; the following derivatives of hydropyrone also undergo the same reaction.

Orthodimethoxydiphenyltetrahydropyronicarboxylic acid (*loc. cit.*) melts at  $140^\circ$  when slowly, and at  $170^\circ$  when rapidly, heated, carbonic anhydride being evolved in each case. Its salts are very unstable, and when warmed in aqueous solution, decompose, forming *o*-dimethoxydiphenyltetrahydropyrone (m. p.  $171^\circ$ ), which is most conveniently obtained from the acid by adding excess of ammonia and evaporating to dryness.

*o*-Diethoxydiphenyltetrahydropyronicarboxylic acid is formed from acetonedicarboxylic acid and orthethoxybenzaldehyde; when quickly heated, it melts at  $170^\circ$ , otherwise at  $140^\circ$ , and when evaporated to dryness with excess of ammonia, gives *o*-diethoxydiphenyltetrahydropyrone,  $\text{CO} \begin{matrix} \text{CH}_2(\text{C}_6\text{H}_4\cdot\text{OEt})\cdot\text{CH} \\ \text{CH}_2(\text{C}_6\text{H}_4\cdot\text{OEt})\cdot\text{CH} \end{matrix} \text{O}$ , which separates from alcohol in white crystals melting at  $126^\circ$ , and is completely converted into the unsaturated ketone,  $\text{CO}(\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , on boiling its alcoholic solution, containing a trace of hydrochloric acid. This ketone forms yellow crystals, melts at  $88^\circ$ , and dissolves easily in alcohol and ether, but is insoluble in water.

J. F. T.

**Structure of Terpenes and Allied Compounds.** By ST. TOL-LOCZKO (*Chem. Centr.*, 1898, i, 105; from *J. russ. chem. Ges.*, 29, 39—63).—In continuation of Wagner's work (*J. russ. chem. Ges.*, 26, 327; 28, 56, 484), the author has obtained a hydrocarbon,  $\text{C}_{20}\text{H}_{36}$ , by the action of sulphuric acid on menthol; it is a colourless, odourless, viscous liquid, which decolorises potassium permanganate with difficulty, and evolves hydrogen bromide when treated with bromine; it boils at  $190$ — $191^\circ$  under 20 mm. pressure, has a sp. gr. of 0.8814 at  $20^\circ/4^\circ$ , 0.8801 at  $22^\circ/4^\circ$ , 0.8944 at  $0^\circ/4^\circ$ , and a refraction coefficient (Pulfrich's refractometer,  $t=22^\circ$ )  $n_D$  1.4841. By the action of sulphuric acid on borneol, the following products are obtained, (1) isocymenesulphonic acid, a liquid which boils at  $162$ — $168^\circ$  and does not decolorise bromine, and (2) a fraction of higher boiling point which distils with difficulty even in a vacuum.

E. W. W.

**Oil of Basil.** By JUSTIN DUPONT and JACQUES GUERLAIN (*Bull. Soc. Chim.*, 1898, [iii], 19, 151—154).—A sample of oil of basil obtained

from the island of Réunion has a rotatory power of  $[\alpha]_D - 12$ , and was proved to consist largely of estragole (paramethoxyallylbenzene); linalool could not be detected. These results have been confirmed by Bertram and Walbaum (*Abstr.*, 1897, i, 625), who have also examined the German oil, and from their analyses, together with the results of the authors' examination of the French oil (*Abstr.*, 1897, i, 429), it appears that specimens obtained from plants cultivated in Europe agree among themselves, but differ greatly in character from the oil from the island of Réunion. N. L.

**Ethereal Oil of Jasmine Flowers. II.** By ALBERT HESSE and FRIEDRICH MÜLLER (*Ber.*, 1899, 32, 765—779. Compare this vol., i, 377).—For the estimation of benzylic alcohol and acetate, linalool and linalyl acetate, their different behaviour towards potassium permanganate is made use of. Benzylic acetate is not attacked in neutral or slightly acid solution, and can be determined in the usual way from the weight of the ethereal salt present in the neutral residue after oxidation; benzylic alcohol is converted quantitatively into benzoic acid, and can be estimated as such, whilst linalool and other terpene-alcohols are oxidised to carbonic and acetic acids, and do not give any solid acid; linalyl acetate and other terpene ethereal salts are oxidised in the same way as the alcohols, and can be estimated from the difference in the weight of ethereal salt present before and after oxidation.

The salts present in jasmine-oil have already been shown to be acetates. Benzylic acetate is readily obtained in a pure state, with the normal composition, boiling point, and density, by oxidation with potassium permanganate, and forms 65 per cent. of the oil. Linalyl acetate and other salts of the terpene series form about 7·5 per cent. of the whole, when determined as the difference between the total quantity of ethereal salts and the weight of benzylic acetate. The benzylic alcohol, determined as benzoic acid after oxidation, amounts to 6 per cent. of the whole. The presence of linalool is somewhat difficult to prove directly; on hydrolysing the oil, the neutral residue gives an inactive fraction of high boiling point, consisting chiefly of benzylic alcohol, and a dextrorotatory fraction of low boiling point, which smells strongly of linalool; a considerable part distils near the boiling point of linalool, but the high density and the formation of benzoic acid on oxidation show that benzylic alcohol is also present, and the difference of boiling point is too small to allow of a complete separation. By the action of formic acid on a fraction of low boiling point, a levorotatory product was obtained which smelt of terpineol, but the lævo-terpineol which is produced from dextro-linalool by this method was not isolated. Similarly, on oxidation with chromic acid, a dextrorotatory product was obtained which smelt of citral, but the latter was not isolated. The quantity of linalool is estimated at 16 per cent., with 5·5 per cent. of other scents. T. M. L.

**French Essence of Peppermint.** By EUGENE CHARABOT (*Bull. Soc. Chim.*, 1898, [iii], 19, 117—120).—The following results were obtained from four specimens of French essence of peppermint:—

	1 1895.	2 1896.	3 1896. Rectified.	4 1896.
Sp. gr. at 18° .....	0.921	0.918	0.918	0.918
Rotatory power at 18° .....	-6°38'	-5°54'	-7°6'	-6°40'
Ethereal salts.....	9.5	10.0	9.8	7.1
Free menthol .....	39.4	35.7	37.8	38.7
Total menthol.....	46.0	43.7	45.5	44.3
Menthone .....	9.0	8.8	9.6	8.9

The ethereal salts were proved to include menthylic acetate and valerate. The French essence differs from the Japanese, American, and English varieties in having a slightly higher density, and a considerably lower rotatory power.

[With EBBAY.]—A peculiar modification of the inflorescence, to which the peppermint plant is subject, was found to be due to the punctures of an insect. The essential oil obtained from such plants has a very coarse odour, and differs considerably in composition from the normal product, as is shown by the following analysis: Sp. gr. 0.924 at 18°; rotatory power, +7°; ethereal salts, 8.2; total menthol, 41.0; menthone, 3.0. N. L.

**Essential Oil of Portugal (Sweet Orange).** By JULIAN FLATAU and H. LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 361—363).—From 500 grams of oil of Portugal, by agitation with saturated sodium hydrogen sulphite solution and decomposition of the precipitate thus obtained with aqueous potash, the authors isolated about 1 gram of a mixture of aldehydic compounds, which included traces of citronellal and 6—7 decigrams of a new *aldehyde* having an odour of oranges. A similar quantity of the oil, when distilled at the ordinary pressure, yielded about 95 per cent of limonene boiling at 177—179°, whilst from the residue, by successive treatment with alcoholic potash and hydrochloric acid, about 6 grams of an oily, unsaturated *acid* was obtained; this readily absorbs 2 mols. of bromine, with the production of a yellow additive *product* which melts at 94—96°. The *silver* salt is a yellow powder, melting at 138—140°, which decomposes on exposure to light; the *barium* salt is a yellowish powder. The analyses of these compounds indicate for the acid a  $C_{21}$ -formula with two ethylenic linkings. The *ethylic* salt, in which form the acid exists in the oil, is best obtained by adding alcohol to the residue left after distillation of the limonene, when it is precipitated in the form of a yellow powder melting at 64—65° and having an odour of oranges; it readily absorbs bromine, with the formation of a pale yellow additive *product* which melts at 56—57°. N. L.

**Essential Oil of Mandarins.** By JULIAN FLATAU and H. LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 364).—A specimen of this oil was found to contain 98 per cent. of limonene, identical with that found in oil of Portugal (see preceding abstract), about 1 per cent. of the ethereal salt also found in that oil, and a trace of citral. N. L.

**Camphor and its Derivatives.** By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], 19, 350—361).—Assuming the validity of the formula

$\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{COOH} \\ \text{CH}_2 \text{---} \text{CH} \cdot \text{COOH} \end{array}$  for camphoric acid, formulæ are deduced for camphor and many of its derivatives. [These formulæ are discussed in a more recent paper by Perkin (*Trans.*, 1898, **73**, 818).]

It is pointed out that the formulæ so obtained for  $\alpha$ - and  $\beta$ -campholenic acids,  $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CHMe} \\ \text{CH} \text{---} \text{C} \cdot \text{CH}_2 \cdot \text{COOH} \end{array}$  and  $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CMe} \\ \text{CH}_2 \text{---} \text{C} \cdot \text{CH}_2 \cdot \text{COOH} \end{array}$  do not explain the formation of isoketocamphoric and isocamphoronic acids from the former, and of dimethylhexanonoic and dimethylglutaric acids from the latter, so well as those suggested by Tiemann, although these are based on what is considered by the author to be an incorrect formula for camphor. Experiments are being carried out with the object of clearing up this point. N. L.

**Camphoric Acid.** By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], **19**, 277—285).—The question of the constitution of camphoric acid is closely connected with that of isolaunonic acid, which is derived from it by the elimination of a carbonyl group and a molecule of water; the author has therefore studied the behaviour of this acid on oxidation. When treated with potassium permanganate and dilute sulphuric acid in the cold, isolaunonic acid is converted into an acid, crystallising in long needles melting at  $132^\circ$  and boiling at  $270^\circ$  under 17 mm. pressure, which is identical with the isolaunonic acid of Königs and Meyer, the constitution of which is unknown. If the oxidation takes place at a higher temperature, an oily acid is obtained which is very soluble in water and boils at  $260^\circ$  under 17 mm. pressure; the study of this compound is not yet completed. When heated at  $100^\circ$  with nitric acid of sp. gr. 1.2, isolaunonic acid yields almost exclusively  $\alpha\alpha$ -dimethylglutaric acid, which was identified by its conversion into the anhydride, anilide, and phenylimide. [Compare Perkin, *Trans.*, 1898, **73**, 842.] N. L.

**Constitution of Camphoric Acid.** By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], **19**, 285—294).—The author examines critically the results obtained by Tiemann, Bredt, Haller, Auwers, Oddo and Manuelli, Balbiano, and Perkin and Thorpe, and discusses their bearing on the question of the constitution of camphoric acid in the light of his own experiments (see preceding abstract). It is urged against Tiemann's formula that it does not account for (1) the profound difference which exists between the two carboxyl groups of camphoric acid, (2) the formation of camphoronic acid by oxidation of camphoric acid, (3) the difference between launonic and isolaunonic acids, (4) the formation of  $\alpha\alpha$ -dimethylglutaric acid by the oxidation of isolaunonic acid, and (5) the optical inactivity of isolaunonic acid. Bredt's formula accords better with the facts, but is inconsistent with the inactivity of isolaunonic acid, and its conversion into  $\alpha\alpha$ -dimethylglutaric acid. Bouveault's formula, on the other hand, explains satisfactorily all the facts known at present. [Compare Perkin, *Trans.*, 1898, 806, *et. seq.*; as to 'Bouveault's formula,' see footnote, *ibid.*, 818.] N. L.

**Molecular Transformations Effected by Hydriodic Acid at High Temperatures.** By G. BLANC (*Bull. Soc. Chim.*, 1898, [iii], 214—218).—The author points out that the results obtained by reducing compounds of the camphor series with hydriodic acid at a high temperature cannot be considered of any value in discussing their structure, owing to the possibility of molecular change occurring; in support of this contention, the results obtained by Markownikoff in the case of cyclic compounds (Abstr., 1897, i, 401) are cited.

When the acid,  $C_{15}H_{20}O_2$ , obtained by Bürcker by acting on camphoric anhydride with benzene in presence of aluminium chloride (Abstr. 1891, 324), is heated (10 grams) with concentrated hydriodic acid of sp. gr. 2.0 (20 c.c.) during successive periods of 5 hours each at the temperatures 100°, 150°, 200°, and 210—220°, a large quantity of naphthalene is formed; a considerable proportion of a liquid boiling at 225—270° is also obtained. This result cannot be explained in a simple manner if the acid has the constitution  $CHPr \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CO} \end{array} CPh \cdot OH$  originally assigned to it (Abstr., 1896, i, 179). W. A. D.

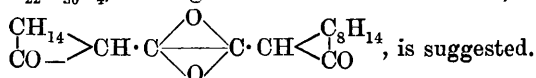
**Action of Ethylic Oxalate on Camphor. IV.** By JOHN BISHOP TINGLE and ALFRED TINGLE (*Amer. Chem. J.*, 1899, 21, 238—261. Compare Abstr., 1897, i, 484; 1898, i, 443, and Trans., 1890, 652).—Improvements have been made in the preparation of camphoroxalic acid by hydrolysing the mixture of borneol, camphor, and ethylic camphoroxalate together in one operation.

*Phenylcamphorformeneamine*,  $\begin{array}{c} \text{CO} \\ | \\ C_8H_{14} \end{array} > C:CH \cdot NHPh$ , is obtained when camphoroxalic acid and aniline, in molecular proportion, are heated at 130° for 30 minutes. It crystallises in colourless, rhombic plates, or occasionally in hair-like needles exceeding an inch in length, melts at 166°, and dissolves readily in alcohol, benzene, or ethylic acetate, but is only sparingly soluble in light petroleum. In alcoholic solution, it gives no coloration with ferric chloride, and when treated with bromine yields a product melting at about 216°. It is not decomposed by boiling with concentrated aqueous sodium hydroxide. The *platinochloride*,  $(C_{17}H_{20}NO)_2 \cdot H_2PtCl_6$ , crystallises in dark orange coloured needles, and is insoluble in water.

*Aniline phenylcamphorformeneaminecarboxylate*,  $C_{17}H_{20}NO \cdot COO \cdot NH_3Ph$ , is formed when solutions of camphoroxalic acid (1 mol.) and aniline (2 mols.) in the smallest possible quantities of warm benzene, are mixed and gently heated on the water-bath; the crystals which separate on cooling are recrystallised from a mixture of benzene and light petroleum. It is extremely unstable in presence of even traces of acid vapours. The acid,  $\begin{array}{c} \text{CO} \\ | \\ C_8H_{14} \end{array} > C:C(NHPh) \cdot COOH$ , is obtained when the aniline salt is triturated with dilute sulphuric or hydrochloric acid; it is also formed by the action of aniline on sodium camphoroxalate. It crystallises from a mixture of benzene and light petroleum in bright yellow needles, melting and decomposing at 174° when quickly heated, and, when heated above its melting point or at

140° in the presence of ethylaniline, yields carbonic anhydride and phenylcamphorformeneamine. It dissolves in sodium carbonate or hydroxide solution, but prolonged boiling with the latter gives aniline and camphoroxalic acid. The *anilide*,  $C_{17}H_{20}NO \cdot CONHPh$ , formed when ethylic camphoroxalate is heated with an excess of aniline at 130° for 3 hours, crystallises from a mixture of benzene and light petroleum in colourless needles and melts at 193°.

When camphoroxalic acid is boiled with benzoic chloride and the product recrystallised from benzene and light petroleum, a substance,  $C_{22}H_{30}O_4$ , melting at 190—191° is obtained, for which the formula



Ethylic camphoroxalate phenylhydrazide, on oxidation with an ethereal solution of hydrogen peroxide, forms two products, of which one crystallises in red needles melting at 210°, and the other melts at 108—109°.

Sodium camphoroxalate, even to the extent of 0.241 gram per kilo. of body weight, has practically no physiological effect. J. J. S.

**Sulphonic Derivatives of Camphor.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1898, [iii], 19, 120—128).—Sulphuric acid alone has little action on camphor at the ordinary temperature, but if coarsely powdered camphor (1 mol.) is added to a well-cooled mixture of acetic anhydride (2 mols.) and sulphuric acid (1 mol.), a liquid product is obtained from which a *camphorsulphonic acid* slowly crystallises, whilst an amorphous isomeric acid may be isolated from the mother liquor.

The crystalline acid, which is shown by analysis and by cryoscopic molecular weight determinations to have the composition  $C_{10}H_{15}O \cdot SO_3H$ , crystallises from acetic acid in large, doubly-refracting, very hygroscopic prisms, which melt and decompose at 193°, and are very soluble in water, slightly so in cold acetic acid, but almost insoluble in ether. The aqueous solution has a rotatory power  $[\alpha]_D = +21^\circ$ , and gives no precipitate with barium chloride, even after boiling with excess of potash or nitric acid. The *ammonium* salt crystallises in small, brilliant prisms, very soluble in water; the *barium* salt forms soluble crystalline crusts. The *normal quinine* salt crystallises in small prisms which are very soluble in water, the solution exhibiting a magnificent blue fluorescence; the *basic quinine* salt is much less soluble, melts in boiling water, and crystallises in long needles. *Camphorsulphonic chloride*,  $C_{10}H_{15}O \cdot SO_2Cl$ , obtained by the action of phosphorus pentachloride on camphorsulphonic acid, crystallises in doubly-refracting plates melting at 67—68°, and is insoluble in water, slightly soluble in light petroleum, readily soluble in ether; it is very slowly acted on by cold, and rather more rapidly by warm water. The *amide*,  $C_{10}H_{15}O \cdot SO_2 \cdot NH_2$ , exists in two distinct modifications, crystallising respectively in plates melting at 220° and in small prisms melting at 125—126°; the *anilide*,  $C_{10}H_{15}O \cdot SO_2 \cdot NHPh$ , prepared by heating the chloride with aniline at 100°, crystallises from alcohol in large, doubly refracting prisms which melt at 119° and are

insoluble in water, soluble in alcohol and ether. *Phenylic camphorsulphonate*,  $C_{10}H_{15}O \cdot SO_3Ph$ , obtained by the action of camphorsulphonic chloride on alcoholic sodium phenoxide, is a thick, oily liquid, insoluble in water. The *oxime*,  $SO_3H \cdot C_{10}H_{15} : NOH$ , prepared by Beckmann's general method, crystallises in large prisms which decompose at  $177-178^\circ$ , and are soluble in water, but less soluble in boiling alcohol. The *phenylhydrazone*,  $OH \cdot SO_2 \cdot C_{10}H_{15} : N_2HPh$ , crystallises in small, brilliant plates which melt and decompose at  $235^\circ$ , and are insoluble in water, but very soluble in aqueous potash; it reduces Fehling's solution slowly in the cold, and rapidly on warming. The action of excess of phenylhydrazine on camphorsulphonic chloride in ethereal solution leads to the formation of a *compound*, possibly  $NHPh \cdot NH \cdot SO_2 \cdot C_{10}H_{15} : N_2HPh$ , which crystallises in slender needles melting at  $149-151^\circ$ . It is insoluble in water, is decomposed with effervescence by warm aqueous potash, and rapidly reduces Fehling's solution in the cold.

The amorphous camphorsulphonic acid which is formed along with, although in smaller quantity than, the isomeric crystalline acid, was obtained only as a yellowish, syrupy mass, extremely soluble in water. The *barium* salt is a yellowish, amorphous, pulverulent substance, whilst the *ammonium* salt was obtained as an amorphous, gummy mass sometimes showing signs of crystallisation on keeping. The *chloride*, which could not be obtained in a pure state, is an insoluble oil. Unsuccessful attempts to prepare a phenylhydrazone seem to show that the amorphous acid does not contain the carbonyl group.

These acids are, therefore, not identical with Kipping and Pope's camphorsulphonic acid (Trans., 1893, 63, 573). N. L.

**Stick-lac.** By ALEXANDER TSCHIRCH and A. FARNER (*Arch. Pharm.*, 1899, 237, 35-48).—The wax was removed from the coarsely powdered lac by extraction with pure light petroleum in a reflux apparatus (compare Benedikt and Ulzer, Abstr., 1888, 1309; Gascard, *J. Chim. Pharm.*, 1893, 365). The residue was extracted with warm water, the aqueous extract concentrated and precipitated with lead acetate; by decomposing the precipitate with sulphuric acid, the crude colouring matter was obtained (compare R. E. Schmidt, Abstr., 1887, 734). Finally, the purified resin was obtained by treating the residual lac with an equal weight of hot alcohol, filtering into 4-5 times the quantity of water, and adding a few drops of dilute hydrochloric acid. The residue insoluble in the alcohol consisted of woody matter, carapaces of insects, colouring matter, &c.

The resin formed a bulky, amorphous, light brown powder. It was dissolved in an equal weight of alcohol, and the solution mixed cautiously with 8-10 times the weight of ether, and then shaken vigorously. The precipitate which formed was washed with ether, dissolved in alcohol, and precipitated by pouring the solution into a large quantity of water and adding a few drops of hydrochloric acid; it forms a white, amorphous powder devoid of acid properties. In order to hydrolyse it, it was dissolved in 10 per cent. caustic potash, and the solution boiled for several hours while a current of steam



was passed through it; the hot solution was then acidified with sulphuric acid, when a crystalline precipitate formed on cooling; this was filtered off and the solution extracted with ether, the process being repeated until only a negligible amount of substance was extracted. The united crystalline precipitates and residues obtained on evaporating the ethereal extracts were then heated with water and excess of magnesium carbonate, the solution was treated with animal charcoal, and the magnesium salt crystallised and decomposed with hydrochloric acid; the acid which separated was recrystallised several times from alcohol and water. It is named *aleuritic acid*; it melts at  $101.5^{\circ}$ , and has the composition  $C_{13}H_{26}O_4$ ; it is a monobasic acid, but forms *magnesium*, *lead*, and *barium* salts of the type  $(C_{12}H_{25}O_2 \cdot COO)_2M'' \cdot C_{12}H_{25}O_2 \cdot COOH$ ; probably it is a dihydroxyundecic acid. The other product of the hydrolysis of the resin could only be obtained as a sticky substance; it appears to be a *resinotannol* (Abstr., 1894, ii, 361), but was probably mixed with fatty acids. The resin insoluble in ether may thus be regarded as the resinotannol salt of aleuritic acid, the two hydroxyl groups of the latter having at the same time condensed with fatty acids. Stick-lac thus resembles amber in the fact that its resin contains fatty acids; all other resins hitherto examined contain only aromatic acids.

The ethereal solution, containing part of the original resin still dissolved, was agitated gently with successive quantities of aqueous 1 per cent. sodium carbonate solution, 20—25 litres being used for 100 grams of the resin; it was impossible to shake vigorously, as the liquids then formed an emulsion. The remaining ethereal solution contains a white substance of the nature of a *resin*; the amount of this equals about  $1\frac{1}{2}$  per cent. of the crude product. The soda solution was precipitated with aqueous lead acetate; the precipitate was suspended in alcohol, warmed, and decomposed with sulphuric acid, and the solution treated with animal charcoal and precipitated with alcoholic lead acetate; a violet lake was precipitated, and the filtrate, when treated with sulphuric acid, yielded a sticky substance with a strong odour of shellac, and apparently consisting of fatty acids; this substance forms the bulk of the resin soluble in ether. The violet lake was decomposed with alcohol and sulphuric acid, and the solution poured into water to precipitate the colouring matter, from which a substance, named *erythrolaccin*, was eventually isolated. It forms about 1 per cent. of the purified resin, is yellow to red in colour; when heated, it decomposes, but sublimes in part; with strong sulphuric acid, it forms a bluish-violet solution, which gives three absorption bands between  $\lambda = 0.640-0.680$ ,  $0.540-0.560$ , and  $0.500-0.525 \mu$ ; it has the composition  $C_{15}H_{10}O_5 + H_2O$ , and appears to be a hydroxymethylantraquinone, most nearly resembling methylquinalizarin of those at present known.

Stick-lac contains wax 6, colouring-matter 6.5, purified resin 74.5 (of which 65 per cent. is insoluble, and the remainder soluble in ether), residue 9.5 and water, &c., 3.5 per cent.

Bleached lac was also examined; like the unbleached material, it contains aleuritic acid, but no wax, and all its constituents contain

considerable quantities of chlorine; moreover, it is not entirely soluble in alcohol, a substance resembling "Lackstoff" being left undissolved. The bleaching of the lac is due to the destruction or alteration of the erythrolaccin.

C. F. B.

**Chemical Constituents of *Fabiana Imbricata*.** By HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1899, 237, 1—35).—*Fabiana imbricata* (Ruiz and Pavon), or Pichi-pichi, is a shrub which occurs in dry districts of Chili, between 29° and 37° S. latitude, and from 1000 to 6500 feet above sea-level; it is one of the *Solanaceæ*, but in adapting itself to its environment it has acquired some of the external characters of the *Coniferae*. Of late years, it has been employed in Europe as a drug, and has been investigated chemically, but not in an exhaustive fashion. The material employed in the present investigation consisted of a syrupy "fluid extract" (alcoholic) and a plastic "extr. spissum," in addition to the drug itself.

The powdered leaves were extracted twice with hot water, then exhausted with ether in a Soxhlet apparatus, and finally extracted with alcohol. The aqueous extract contained magnesium phosphate, which was precipitated on adding ammonia; from the filtrate, lead acetate precipitated *fabianaglutotannoid* mixed with a little chrysotropic acid; after these were removed, potassium mercuri-iodide precipitated choline (no other alkaloid could be detected), and on removing this and adding common salt, a soft, resinous substance was thrown down, whilst from the residual solution, ether extracted a liquid that appeared to contain formic acid, but consisted mainly of the same *resin*; this resin is apparently the parent substance of all the compounds obtained; when boiled with dilute sulphuric acid, it yields *fabianol*, chrysotropic acid, and a *sugar* which reduces Fehling's solution, but is optically inactive, and was not obtained crystallised. The ethereal extract yielded *fabianol* when distilled with steam; by adding ammonia to the residue and diluting with water, a precipitate of *fabianaresen* was obtained, and from the filtrate from this, after acidification with sulphuric acid, chloroform extracted chrysotropic acid (4-hydroxy-5-methoxycoumarole,  $C_{10}H_8O_4$ ) melting at 204°. The alcoholic extract contained *fabianaglutotannoid*, choline, and a trace of substance smelling like vanillin.

The powdered wood was extracted with alcohol and ether successively; the alcoholic extract contained chrysotropic acid and choline; the ethereal extract chrysotropic acid and a substance which formed acraldehyde when heated with "primary" potassium sulphate.

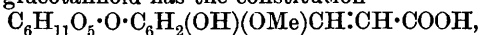
The commercial extracts were freed from alcohol, and extracted with water; the aqueous extract contained chrysotropic acid, choline, *fabianaglutotannoid* and—after boiling with 1 per cent. sulphuric acid—*fabianol*; from the residue, *fabianol* could be distilled over with steam, while *fabianaresen* was left behind. A somewhat larger yield of *fabianol* was obtained by dissolving the original extract in caustic soda and distilling with steam; the residue, after acidification, had a distinct odour of butyric acid.

If it is desired to obtain the *glucotannoid* and *resen* only, it is best to extract the leaves with chloroform and hot water successively; the

chloroform extract yields fabianaresen, which is washed with cold dilute alcohol and crystallised from boiling alcohol, animal charcoal being employed to effect decolorisation; the aqueous extract, when evaporated, leaves fabianaglutotannoid, which is purified by dissolving it in a little water and precipitating it with alcohol, the process being repeated several times.

*Fabianaresen* is a white, crystalline substance which melts at about  $280^{\circ}$  and can be sublimed; on chemical grounds, the author prefers the formula  $C_{54}H_{90}O_6$  for it, although a cryoscopic determination of the melting point is in accordance with the simpler formula,  $C_{18}H_{30}O_2$ . When it is treated with bromine in ethereal or alcoholic solution, a colourless bromo-derivative,  $C_{18}H_{28}Br_2O_2$  is formed, which can be obtained crystallised; when boiled with bromine in acetic acid solution, it yields a yellow product, apparently a mixture of perbromides; the colourless bromo-derivative may be obtained from this by dissolving it in the minimum quantity of benzene and diluting the solution with 50 per cent. alcohol. Boiling with acetic acid has no effect on fabianaresen, but by heating it with acetic anhydride and sodium acetate at  $120^{\circ}$ , it can be made in part to yield an *acetyl* derivative,  $C_{18}H_{29}AcO_2$ , which melts at  $234^{\circ}$  after softening at  $215^{\circ}$ . When heated with benzoic anhydride at  $150$ – $160^{\circ}$ , it yields a *benzoyl* derivative,  $C_{18}H_{29}BzO_2$ , which melts at  $61^{\circ}$ . Sodium has little action on fabianaresen in chloroform solution; hydriodic acid of sp. gr. 1.7 and phosphorus at  $250^{\circ}$  reduce it to a waxy substance,  $C_{54}H_{98}O_2$ , the formation of which is most simply explained by adopting the triple formula for fabianaresen. The resen is not affected by boiling with alcoholic potash; when it is fused with a mixture of potassium and sodium hydroxides, a product is obtained which melts at  $178$ – $180^{\circ}$  after softening at  $125^{\circ}$ , is acid in character, and in its colour reactions with concentrated sulphuric acid resembles hesperetol (vinylparamethoxycatechol) and vinylcatechol (Abstr., 1894, ii, 328).

*Fabianaglutotannoid* is a yellow, very hygroscopic substance, which reduces alkaline silver and copper solutions; it softens at  $80^{\circ}$  and begins to swell up at about  $105^{\circ}$ ; it exhibits many of the reactions of the tannic acids of maté and coffee. It contains C 42.30 and H 5.65; if it is distilled with aqueous potash, the distillate yields iodoform when treated with potash and iodine solution, and the residual substance is no longer hygroscopic; with bromine water, an orange precipitate, apparently of dibromomethoxydihydroxycinnamic acid, is obtained. Possibly the glutotannoid has the constitution



or is an intramolecular anhydride of this; its yellow *lead* and green *copper* salts have a percentage of metal corresponding with that required for the basic formula  $C_{32}H_{36}O_{20}M'_2 + 2H_2O$ , and, although insoluble in water, are soluble even in very weak acids and alkalis. C. F. B.

The Quinquevalent Asymmetric Nitrogen Atom. III. 1-Hydroxypiperidiniumacetic Acid. By EDGAR WEDEKIND (Ber., 1899, 32, 722–728. Compare this vol., i, 357).—Hydroxypiperidiniumacetic acid,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{NH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared

by the action of chloracetic acid on aqueous piperidine (Kraut), or by hydrolysing ethylic piperidylacetate (Bischoff and Stefanowski, this vol., i, 229), separates from alcohol in sphenoidal, hemihedric crystals belonging to the rhombic system;  $[a:b:c=0.9462:1:0.5887]$ . Although both enantiomorphous forms are produced on crystallisation from alcohol (compare Miss Evans, Trans., 1897, 71, 522), the fractions consist almost exclusively of left-handed crystals; these are optically inactive, and although capable of supporting a culture of *Penicillium glaucum*, an aqueous solution which has been submitted to the influence of the organism during three weeks remains inactive at the end of this period.

Attempts to substitute alkyl groups for the hydrogen attached to the nitrogen atom in hydroxypiperidiniumacetic acid result in the production of ammonium salts of the corresponding halogen hydrides; when these are treated with silver oxide, hydroxypiperidiniumacetic acid is regenerated. M. O. F.

**Ammonium Salt of Ethylic 2:6-Dihydroxynicotinate.** By MAX GUTHZEIT (*Ber.*, 1899, 32, 779—782).—The compound prepared by Errara by boiling an alcoholic solution of diethylic  $\alpha$ -dicyanoglutaconate (Abstr., 1898, i, 297), and formulated as the diamide of diethylic dicarboxyglutaconate,

$\text{COOEt} \cdot \text{CH}(\text{CO} \cdot \text{NH}_2) \cdot \text{CH} : \text{C}(\text{CO} \cdot \text{NH}_2) \cdot \text{COOEt}$  (*ibid.*, 490), is shown to be identical with the ammonium salt of ethylic dihydroxynicotinate  $[\text{OH} : \text{COOEt} : \text{COOEt} : \text{OH} = 2 : 3 : 5 : 6]$ . The latter is, however, a monobasic acid, the *silver* and *copper* salts being described in addition to the sodium and ammonium salts, and the author, therefore, regards it as being the ketonic form,  $\text{COOEt} \cdot \text{C} \cdot \text{CH} : \text{C} \cdot \text{COOEt}$ , and not  $\text{OH} \cdot \text{C} \cdot \text{NH} \cdot \text{CO}$ , and not

a normal pyridine derivative.

T. M. L.

**Action of Alkylid Iodides on Indoles. Action of Ethylic Iodide on 2-Methylindole (Methylketole).** By GIUSEPPE PLANCHER (*Gazzetta*, 1898, 28, ii, 333—373).—Fischer and Steche, and Ciamician and Plancher, have shown that, by ethylating methylketole, three products are obtained having the formulæ  $\text{C}_{11}\text{H}_{13}\text{N}$ ,  $\text{C}_{18}\text{H}_{17}\text{N}$ , and  $\text{C}_{15}\text{H}_{21}\text{N}$ . The first of these, to which the name 2'-methyl-1'-ethylindole has been given, the author has identified with 2'-methyl-3'-ethylindole,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CEt} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CMe}$ , obtained by Fischer by condensing the phenylhydrazone of methyl propyl ketone by means of zinc chloride; it is a dense, colourless liquid boiling at 192—195° under 50 mm. pressure, and forms a picrate melting at 152—153°.

The second ethylation product, which can also be obtained by the action of ethylic iodide on 2'-methyl-3'-ethylindole, has been formerly regarded as a dihydroquinoline derivative of the constitution

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CEt}_2 \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{CH}$ ; the fact that it is stable towards permanganate tends to show that the double linking exists, not between two carbon atoms, but between a carbon and a nitrogen atom, as is the case with the oximes and with benzylideneaniline, and the author finds that the compound is really 2'-methyl-3':3'-diethylindolenine,

$C_6H_4 \langle \begin{smallmatrix} CEt_2 \\ N \end{smallmatrix} \rangle CMe$ . It is produced from 2'-methyl-3'-ethylindole by the direct addition of ethylic iodide and the splitting off of hydrogen iodide. It forms a sparingly soluble picrate melting at 189—190°, which serves for its separation. When 2'-methyl-3':3'-diethylindolenine is acted on by hot permanganate solution, its 2'-methyl group is oxidised, giving rise to 3':3'-diethylindolenyl-2'-carboxylic acid,  $C_6H_4 \langle \begin{smallmatrix} CEt_2 \\ N \end{smallmatrix} \rangle C \cdot COOH$ , which melts at 125° with loss of carbonic

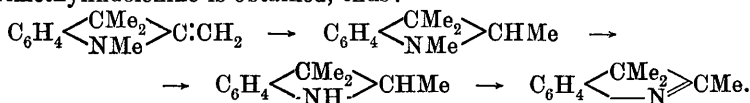
anhydride and formation of 2':2'-diethylindolenine,  $C_6H_4 \langle \begin{smallmatrix} CEt_2 \\ N \end{smallmatrix} \rangle CH$ ; this compound, like the homologous dimethyl base obtained by Brunner (Abstr., 1896, i, 169 and 625), forms, with methylic iodide, an additive compound,  $C_{12}H_{15}N, MeI$ , melting with decomposition at 132°. When this methiodide is acted on by potassium hydroxide, its iodine is replaced by hydroxyl, forming 1'-methyl-3':3'-diethylindolinol,  $C_6H_4 \langle \begin{smallmatrix} CEt_2 \\ NMe \end{smallmatrix} \rangle CH \cdot OH$ ; this substance, which has a pungent odour, is soluble in ether and melts at 55°; it is a homologue of Brunner's trimethylindolinole, for bromine water oxidises and brominates it, giving the dibromo-derivative of 1'-methyl-3':3'-diethylindolinone,  $C_6H_2Br_2 \langle \begin{smallmatrix} CEt_2 \\ NMe \end{smallmatrix} \rangle CO$ , which melts at 92—93° and separates from light petroleum in orthorhombic crystals; [ $a:b:c = 0.45907:1:1.38622$ ].

On treating 2'-methyl-3'-ethylindole with methylic iodide, the compound formerly known as 1'-methyl-4':4'-diethyldihydroquinoline is obtained; the author's researches show this to be 1'-methyl-3':3'-diethyl-2'-methylenindoline. It is a liquid lighter than water, and boils at 147—150° under 25 mm., and at 257—260° under 753 mm. pressure; by sodium and alcohol, it is reduced to 1':2'-dimethyl-3':3'-diethylindoline,  $C_{14}H_{21}N$ , which boils at 154—158° under 25 mm. pressure, and forms a platinumchloride,  $(C_{14}H_{21}N)_2, H_2PtCl_6$ , melting and decomposing above 200°. When treated with phosphorus and hydriodic acid, this reduced base yields 2'-methyl-3':3'-diethylindoline,  $C_{13}H_{19}N$ , which melts at 217° and gives a picrate forming triclinic crystals melting at 138°; [ $a:b:c = 1.97272:1:1.41341$ ;  $\alpha = 113^\circ 36'$ ,  $\beta = 111^\circ 30'$ ,  $\gamma = 63^\circ 18'$ ]. The same base,  $C_{13}H_{19}N$ , is obtained on reducing 2'-methyl-3':3'-diethylindolenine.

From 2'-methyl-3'-ethylindole, the analogous 1':3':3'-triethyl-2'-methylenindoline,  $C_6H_4 \langle \begin{smallmatrix} CEt_2 \\ NEt \end{smallmatrix} \rangle C \cdot CH_2$ , is obtained by substituting ethylic for methylic iodide; it is the third ethylation product of methylketole. It is a colourless, mobile liquid boiling at 265° under 760 mm. pressure, and reddens on long exposure to the air; its picrate crystallises from absolute alcohol in pale yellow, monoclinic prisms melting at 119—120°; [ $a:b:c = 0.84090:1:0.63396$ ;  $\beta = 70^\circ 51'$ ]. This base, and the corresponding methyldiethyl compound described above, are readily oxidised by permanganate solution.

Of similar constitution to these two indoline derivatives is the compound formerly described under the name trimethyldihydroquinoline,

and hence must be 1':3':3'-trimethyl-2'-methylenindoline; if it is submitted first to reduction, then to demethylation by means of hydriodic acid, and finally to oxidation with permanganate, 1':3':3'-trimethylindolenine is obtained, thus:



When heated with sodium acetate and acetic anhydride, 2'-methyl-3':3'-diethylindolenine yields an acetyl compound derived from its tautomeric form and having the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CEt}_2 \\ \text{NAc} \end{array} > \text{C}:\text{CH}_2$ .

On heating in a closed tube with acetic anhydride, this acetyl derivative is converted into an isomeric form, probably of the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CEt}_2 \\ \text{N} \end{array} > \text{C}:\text{CH}_2\text{Ac}$ ; this separates from light petroleum in colourless triclinic crystals melting at 113–114°; [ $a:b:c = 1.080084:1:0.73202$ ;  $\alpha = 83^\circ 28'$ ,  $\beta = 102^\circ 13'$ ,  $\gamma = 98^\circ 54'$ ]. On boiling the latter acetyl compound with dilute hydrochloric acid, it is converted into 2'-methyl-3':3'-diethylindolenine. T. H. P.

**Action of Alkylidic Iodides on Indoles.** 1':3'-Dimethyl-3'-ethyl-2'-methylenindoline. By GIUSEPPE PLANCHER (*Gazzetta*, 1898, 28, ii, 374–391).—By the action of ethylic iodide on 1':2':3'-trimethylindole, Ciamician and Boeris (*Abstr.*, 1897, i, 102) obtained a tertiary base of the composition  $\text{C}_{13}\text{H}_{17}\text{N}$ , which, according to the author's views, must be 1':3'-dimethyl-3'-ethyl-2'-methylenindoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMeEt} \\ \text{NMe} \end{array} > \text{C}:\text{CH}_2$ , and should also be formed by the interaction of 2'-methyl-3'-ethylindole and methylic iodide; the author has shown that these two reactions give rise to one and the same base. The picrate,  $\text{C}_{13}\text{H}_{17}\text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ , crystallises from alcohol in golden-yellow scales melting at 113–114°. The benzoyl derivative,  $\text{C}_{13}\text{H}_{16}\text{NBz}$ , crystallises from light petroleum in monoclinic prisms melting at 119–120°; the crystallographic constants of the benzoyl derivatives of the bases obtained by these two methods are as follows:—(1) From the trimethylindole; [ $a:b:c = 0.93529:1:0.60169$ ;  $\beta = 89^\circ 23'$ ]. (2) From the ethylmethylindole; [ $a:b:c = 0.93637:1:0.60446$ ;  $\beta = 89^\circ 26'$ ].

On oxidation with alkaline permanganate, this tertiary base gives rise to the 1':3'-dimethyl-3'-ethylindolinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMeE} \\ \text{NMe} \end{array} > \text{CO}$ , as this, on treatment with bromine water, gives the dibromo-derivative,  $\text{C}_{12}\text{H}_{15}\text{NBr}_2\text{O}$ , which is soluble in the ordinary organic solvents, and crystallises from dilute acetic acid in monoclinic needles melting at 121–122°; [ $a:b:c = 2.36199:1:2.97023$ ;  $\beta = 82^\circ 39'$ ].

When heated with zinc chloride, the phenylhydrazone of diethylketone condenses, forming 3'-methyl-2'-ethylindole,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe} \\ \text{NH} \end{array} > \text{CEt}$ , which crystallises from light petroleum in colourless plates melting at

66°; it forms a picrate crystallising in red needles melting at 150—151°, and a nitroso-derivative which shows Liebermann's colour reaction for nitrosamines.

By the action of methylic iodide on 3'-methyl-2'-ethylindole, 1':3'-dimethyl-3'-ethyl-2'-methylenindoline is formed, its identity with the compounds obtained from 1':2':3'-trimethylindole and from 2'-methyl-3'-ethylindole being established by the crystal measurements of its benzoyl derivative. T. H. P.

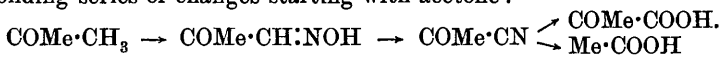
**Action of Alkylid Iodides on Indoles.** **Action of Methylic Iodide on 2'-Phenylindole.** By GIUSEPPE PLANCHER (*Gazzetta*, 1898, 28, ii, 391—403).—When methylic iodide acts on 2'-phenylindole,  $C_6H_4<\begin{smallmatrix} CH \\ NH \end{smallmatrix}>CPh$ , a hydriodide of the composition  $C_{17}H_{17}N, HI$ , is obtained, which crystallises in almost colourless prisms melting with decomposition at 226—227°. It is very soluble in hot methylic or ethylic alcohol, from which it is precipitated by ether or ethylic acetate; it is also slightly soluble in water. Digestion of this hydriodide with solutions of alkalis liberates the base, 3'-phenyl-1':3'-dimethyl-2'-methylenindoline,  $C_6H_4<\begin{smallmatrix} CMePh \\ NMe- \end{smallmatrix}>C:CH_2$ , which separates from light petroleum in crystals melting at 104—105° and is readily oxidised by permanganate in either acid or alkaline solution, although no definite products have as yet been isolated. The *platinochloride*,  $(C_{17}H_{17}N)_2, H_2PtCl_6$ , melts and decomposes at 223—224°. The *acetyl derivative*,  $C_6H_4<\begin{smallmatrix} CMePh \\ NMe- \end{smallmatrix}>C:CHAc$ , separates from ethylic acetate in yellowish, triclinic crystals melting at 142° [ $\alpha:b:c = 0.81919:1:0.86421$ ;  $\alpha = 102^\circ 6'$ ,  $\beta = 106^\circ 58'$ ,  $\gamma = 89^\circ 27'$ ], and the *benzoyl derivative*,  $C_{17}H_{16}NBz$ , crystallises from ethylic acetate and melts at 141°; both these derivatives are stable towards permanganate.

On reducing the base with tin and hydrochloric acid, it is converted into 3'-phenyl-1':2':3'-trimethylindoline,  $C_6H_4<\begin{smallmatrix} CMePh \\ NMe- \end{smallmatrix}>CHMe$ , which separates as a colourless oil; it gives a hydriodide,  $C_{17}H_{19}N, HI$ , which forms colourless crystals melting at 227—228°, and dissolves in water or alcohol slightly in the cold, moderately on heating. The reduced base is completely demethylated by heating with phosphorus and hydriodic acid. T. H. P.

**Action of Alkylid Iodides on Indoles.** **Action of Nitrous Acid on 2'-Methyl-3':3'-diethylindolenine.** By GIUSEPPE PLANCHER (*Gazzetta*, 1898, 28, ii, 405—418).—On treating a cold glacial acetic acid solution of 2'-methyl 3':3'-diethylindolenine with a slight excess of aqueous potassium nitrite, 3':3'-diethylindolenine-2'-formoxine,  $C_6H_4<\begin{smallmatrix} CEt_2 \\ N \end{smallmatrix}>C:CH \cdot NOH$ , is produced; it forms silky needles melting at 169°, and is soluble in alcohol, readily so in boiling benzene, but is only slightly dissolved by light petroleum or by water. It dissolves in dilute caustic alkali with a yellow coloration, and from its solution in concentrated mineral acids or in glacial acetic acid, it is precipitated unchanged by dilution or by neutralisation with

alkali carbonates. In cold alcoholic solution, it is stable towards 2 per cent. aqueous permanganate, but on rendering alkaline it is immediately oxidised. Cryoscopic examination of its solution in phenol shows that its molecular weight corresponds with that required for the formula  $C_{13}H_{16}N_2O$ . The oxime gives a crystalline benzoyl derivative, and on heating with five times its weight of acetic anhydride, forms an *acetyl* derivative,  $C_6H_4 \langle \text{CEt}_2 \rangle_N C \cdot CH \cdot NOAc$ , which crystallises from dilute alcohol in well-defined, transparent laminæ melting at  $100^\circ$ . If the heating with acetic anhydride is continued, 3':3'-*diethylindolenine-2'-nitrile*,  $C_6H_4 \langle \text{CEt}_2 \rangle_N C \cdot CN$ , is obtained in quantitative yield. It is a colourless, mobile liquid, with a pleasing odour, and boils at  $163\text{--}164^\circ$  under 27 mm. pressure. The ordinary organic solvents and water dissolve it, and it is not hydrolysed by acids or by caustic alkalis. When mixed with equivalent quantities of hydroxylamine hydrochloride and sodium carbonate and gently heated, 3':3'-*diethylindolenine-2'-formamidoxime*,  $C_6H_4 \langle \text{CEt}_2 \rangle_N C \cdot C \begin{smallmatrix} \text{NOH} \\ \text{NH}_2 \end{smallmatrix}$ , is obtained; this melts at  $121\text{--}122^\circ$ , and crystallises from alcohol in colourless needles or prisms arranged in rows or crosses. On hydrolysing the nitrile with alcoholic potash, two products are obtained. The first is the corresponding 3':3'-*diethylindolenine-2'-carboxylic acid*,  $C_6H_4 \langle \text{CEt}_2 \rangle_N C \cdot COOH$ , which is identical with the acid obtained from 3':3'-*diethyl-2'-methylindolenine* by oxidation with permanganate. The second product is 3':3'-*diethylindolinone*, having the tautomeric formulæ  $C_6H_4 \langle \text{CEt}_2 \rangle_N COH$ , and  $C_6H_4 \langle \text{CEt}_2 \rangle_{NH} CO$ ; it melts at  $157\text{--}158^\circ$ , and forms a dibromo-derivative,  $C_{12}H_{13}NOBr_2$ , which separates from dilute alcohol in colourless crystals melting at  $171^\circ$ .

The author calls attention to the similarity of the two groups,  $\cdot N \cdot CMe \cdot$  and  $\cdot O \cdot CMe \cdot$ , contained in the indolenines and in acetone respectively, and suggests that the transformations of 3':3'-*diethyl-2'-methylindolenine* into oxime, thence into nitrile, and the hydrolysis of the latter into two different products, are analogous to the corresponding series of changes starting with acetone:



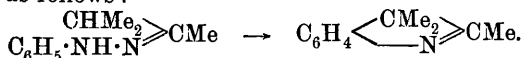
T. H. P.

**Synthesis of the Bases formed by the Methylation of Indole.** By GIUSEPPE PLANCHER (*Gazzetta*, 1898, 28, ii, 418—433).—The author has confirmed his views (Abstr., 1898, i, 536) regarding the constitution of 2':3':3'-*trimethylindolenine* and 1':3':3'-*trimethyl-2'-methylenindolenine*, by preparing them synthetically from the phenylhydrazone of isobutaldehyde by Brunner's method (Abstr., 1896, i, 169 and 625).

When the phenylhydrazone of methyl isopropyl ketone is heated in alcoholic solution with zinc chloride, it is converted into 2':3':3'-*trimethylindolenine*, identical in all its properties with the base



obtained by oxidising 2':3':3'-trimethylindoline; the condensation takes place as follows:—



This shows that Brunner's process permits of extension to ketones having a  $\cdot\text{CH}\cdot$ -group joined to the carbonyl and that in the case of the phenylhydrazone of a ketone having a  $\cdot\text{CH}\cdot$  and a  $\text{CH}_3$ -group joined to the carbonyl, the hydrogen of the former is expelled in preference to that of the latter. The action of methylic iodide on the above trimethylindolenine and the condensation of the methyl-phenylhydrazone of methyl isopropyl ketone both yield 1':3':3'-trimethyl-2'-methylenindoline, identical with Fischer's trimethyldihydroquinoline.

By heating the phenylhydrazone of di-isopropyl ketone in presence of zinc chloride, it condenses to 3':3'-dimethyl-2'-isopropylindolenine,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{CPr}^i$ , which crystallises from light petroleum in prisms, melts at  $80^\circ$  and boils at  $250\text{--}260^\circ$ ; it is hydrolysed even by dilute acids, is stable towards permanganate, and in benzene has the normal molecular weight. On methylation, it yields 1':3':3'-trimethyl-2'-isopropylidenindoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N}^{\text{Me}} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{C}:\text{CMe}_2$ , identical with the pentamethyldihydroquinoline obtained by Zatti and Ferratini (Abstr., 1890, 1292), and by Piccinini (this vol., i, 76); this forms a hydriodide melting with decomposition at  $185^\circ$ , and an aurichloride which separates from dilute hydrochloric acid in yellow crystals melting at  $150^\circ$ , also with decomposition. T. H. P.

**Constitution of Bases formed by the Action of Alkylid Iodides on Indoles.** By GIUSEPPE PLANCHER and D. BETTINELLI (*Real. Accad. Linc.*, 1898, i, 367—372. Compare Abstr., 1898, i, 536).—It has previously been shown that the so-called trimethyldihydroquinoline has most probably the constitution  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N}^{\text{Me}} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{C}:\text{CH}_2$ , but the formulæ  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N}(\text{CH}_2) \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{CMe}$  and  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \\ \text{---} \end{array} \text{N} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{CH}_2$  have also been suggested for this compound. If trimethyldihydroquinoline is represented either by the second or third formula, tetramethyldihydroquinoline, having similar properties, must be either  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N}(\text{CHMe}) \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{CMe}$  or  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \\ \text{---} \end{array} \text{N} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{CHMe}$ , and since trimethyldihydroquinoline is obtained by the action of methylic iodide on 2':3':3'-trimethylindolenine,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{CMe}$ , it follows that the base formed by the action of ethylic iodide on the same indolenine would in either case be identical with tetramethyldihydroquinoline. This, however, is found not to be the case, the product of the reaction being the hydriodide of a new base, 3':3'-dimethyl-1'-ethyl-2'-methyleneindoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CMe}_2 \\ \text{---} \end{array} \text{N}^{\text{Et}} \begin{array}{c} \text{---} \\ \text{---} \end{array} \text{C}:\text{CH}_2$ , which crystallises from alcohol in colourless scales melting at  $219^\circ$ , and from which the base can be

set free with potash. The latter turns red on exposure to air, is lighter than water, almost odourless, and readily soluble in dilute acids; it forms a *picrate*, crystallising in yellowish scales melting at 125°, and a *benzoyl* derivative which crystallises in prisms melting at 140°.

N. L.

**4-Nitrocinchonic Acid and 4-Amidocinchonic Acid.** By WILHELM KOENIGS and EMIL LOSSOW (*Ber.*, 1899, 32, 717—720).—4-Nitroquinoline-4'-carboxylic acid,  $\text{NO}_2 \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{COOH}$ , prepared by treating cinchonic acid with a mixture of concentrated sulphuric and fuming nitric acids at 60—70°, melts and decomposes at 275—278°; it dissolves with great difficulty in water, dilute acids, and in different organic solvents, but is readily dissolved by hot glacial acetic and concentrated hydrochloric acids. The *barium* salt crystallises in yellow needles, and the *calcium* and *ammonium* salts are also crystalline; the *silver* salt is amorphous. When nitrocinchonic acid is distilled with silver powder, 4-nitroquinoline is produced; reduction with stannous chloride converts it into the anhydride of 4-amidocinchonic acid.

The *anhydride* of 4-amidocinchonic acid,  $\text{C}_9\text{H}_5\text{N} \begin{smallmatrix} \text{NH} \\ \diagup \\ \text{CO} \end{smallmatrix}$  or  $\text{C}_9\text{H}_5\text{N} \begin{smallmatrix} \text{N} \\ \diagup \\ \text{C} \cdot \text{OH} \end{smallmatrix}$ , crystallises from water and alcohol in slender yellow needles and melts at 254—255°; it dissolves in cold solutions of caustic alkalis, developing a red coloration, and is precipitated by carbonic anhydride. When boiled with excess of barium hydroxide in a reflux apparatus during 3—4 hours, it yields *barium* 4-amidocinchonate, which forms a yellow, crystalline precipitate; the *acid*, obtained by decomposing the *silver* salt with hydrogen sulphide, crystallises in lustrous red needles.

M. O. F.

**Condensation of Semicarbazide with  $\beta$ -Diketones.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, [iii], 19, 77).—Semicarbazide readily interacts with acetylacetone with elimination of  $2\text{H}_2\text{O}$ , to form a beautifully crystalline *substance*,  $\text{C}_8\text{H}_9\text{N}_2$ , which melts at 107—108°, and probably has the structure of a pyrazole derivative,  $\text{CMe}=\text{N} \begin{smallmatrix} \text{CH}:\text{CMe} \\ \diagup \\ \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$ . It appears probable therefore that the substance,  $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}$ , melting at 192—193°, which was formerly obtained by acting with semicarbazide on the ketone  $\text{C}_{10}\text{H}_{16}\text{O}_2$  (*Compt. rend.*, 1896, 22, 1422) is not a semicarbazone, but a derivative of the above type.

W. A. D.

**Conversion of Secondary Acid Hydrazides into Derivatives of Furodiazole, Pyrrodiazole, and Thiodiazole.** By ROBERT STOLLE (*Ber.*, 1899, 32, 797—798).—The secondary acid hydrazides of the type  $\text{R} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{R}$ , are converted on treatment with dehydrating agents, alcoholic ammonia, or phosphorus pentasulphide into derivatives of furodiazole, pyrrodiazole, or thiodiazole respectively.

*Dimethylfurodiazole*,  $\text{N}:\text{CMe} \begin{smallmatrix} \text{N}:\text{CMe} \\ \diagup \\ \text{O} \end{smallmatrix}$ , is obtained by heating diacetyl-

hydrazine (this vol., i, 413) with zinc chloride or phosphoric anhydride; it can also be prepared by heating tetracetylhydrazine. It is a colourless liquid, boiling at 178—179°, and miscible with water, alcohol, or ether, in all proportions.

*Dimethylpyrrodiazole*,  $\begin{matrix} \text{N}:\text{CMe} \\ \text{N}:\text{CMe} \end{matrix} > \text{NH}$ , is prepared by heating di- or tetracetylhydrazine with alcoholic ammonia at 200°, or by heating a mixture of diacetylhydrazine and zinc ammonium chloride at 250°. It is a white substance, melts at 141—142°, boils at 159° under 19 mm. pressure, and is easily soluble in water, alcohol, and ether.

*Dimethylthiodiazole*,  $\begin{matrix} \text{N}:\text{CMe} \\ \text{N}:\text{CMe} \end{matrix} > \text{S}$ , obtained by heating diacetylhydrazine with phosphorus pentasulphide, is a white, crystalline solid, melting at 64° and boiling at 89° under 14 mm. pressure; it is readily soluble in water, alcohol, and ether.

From dibenzoylhydrazine, diphenylfurodiazole boiling at 231° under 13 mm. pressure, diphenylpyrrodiazole, Pinner (Abstr., 1897, i, 637), and diphenylthiodiazole were prepared.

*Diphenylthiodiazole*,  $\begin{matrix} \text{N}:\text{CPh} \\ \text{N}:\text{CPh} \end{matrix} > \text{S}$ , crystallises from alcohol in glistening leaflets, melts at 141—142°, boils at 259° under 17 mm. pressure, and is insoluble in water. J. F. T.

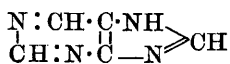
**Synthesis of Indazoles and Phenotriazines.** By A. KÖNIG and ARNOLD REISSERT (*Ber.*, 1899, 32, 782—793).—*Orthonitrobenzophenylhydrazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$ , crystallises from chloroform or alcohol in orange-coloured needles, is only slightly soluble in ether, light petroleum, and water, and melts at 141°; like benzophenylhydrazide, it dissolves in hot caustic soda and ammonia, and is precipitated again by acids; it gives a violet coloration when warmed with concentrated sulphuric acid. The substance also exists in a white modification, and on crystallising from alcohol, both forms usually separate together, but after being for some time in contact with the solution, the white form passes completely into the yellow form. *Orthamidobenzophenylhydrazide* is a colourless base; when acted on with 2 mols. of nitrous acid, it gives an unstable, reddish, crystalline diazo-compound, probably  $\text{OH} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh} \cdot \text{NO}$ . When this is boiled with alcohol, it loses nitrogen and nitrous acid, and is converted into 1'-phenylisindazolone,  $\text{C}_6\text{H}_4 < \begin{matrix} \text{CO} \\ \text{NPh} \end{matrix} > \text{NH}$ , and a small quantity of 3'-anilido-β-phenotriazone,  $\text{C}_6\text{H}_4 < \begin{matrix} \text{CO} \cdot \text{N} \cdot \text{NHPh} \\ \text{N}=\text{N} \end{matrix} >$ , which is separated by its insolubility in caustic soda, crystallises in yellow needles, and melts at 135°.

1'-Phenylisindazolone is stable, crystallises from alcohol in brown needles, melts at 209°, and is fairly soluble in ether and in boiling alcohol, less so in acetone and benzene, and only slightly in water. It is not reduced by sodium in alcoholic solution, and is not attacked by phosphorus pentachloride at 150°; it forms a monobasic, yellowish sodium salt which crystallises with 5H<sub>2</sub>O. The benzoyl derivative

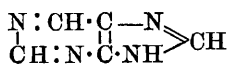
crystallises in colourless needles and melts at  $89^{\circ}$ . The *methyl*-derivative crystallises from dilute alcohol in long, thin, colourless, glistening, monohydrated needles, and melts at  $54-55^{\circ}$ ; it is insoluble in water, but dissolves in alcohol or ether. When oxidised with potassium permanganate, 1'-phenylisindazolone is converted into *nitrosodiphenylamineorthocarboxylic acid* (or *thonitrosoanilidobenzoic acid*),  $\text{NO} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ ; this separates from benzene in yellow crystals containing 1 mol. of benzene of crystallisation, dissolves readily in alcohol, ether, and acetone, but only slightly in water and light petroleum, and melts at  $120-125^{\circ}$ ; the *silver* salt is yellow. On reducing it with zinc dust and acetic acid, Graebe and Lagodzinski's phenylanthranilic acid is produced (Abstr., 1892, 1086).

*Orthonitrophenylacetanilide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ , crystallises from alcohol in needles, dissolves readily in acetone, only slightly in ether and benzene, is insoluble in water, and melts at  $158-159^{\circ}$ . *Orthamidophenylacetanilide*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$  is produced in small quantity by the reduction of the nitro-compound, oxindole being the chief product; it separates from dilute alcohol and from benzene in colourless crystals and melts at  $132^{\circ}$ . T. M. L.

**Syntheses in the Purine Group.** By EMIL FISCHER (*Ber.*, 1899, 32, 435—504).—This paper is a summary of the results obtained by the author, more particularly in his recent researches. After an historical introduction, the question of the structure and nomenclature of these diureides is considered. They are best regarded, as indeed has been done of late, as derivatives of *purine*, all containing as a nucleus a combination of a metadiazine with an imidazole ring. For purine itself, two tautomeric formulæ are possible:

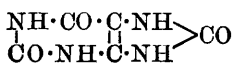


Purine.

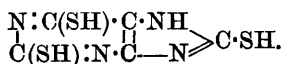


Tautomeric formula.

In the case of derivatives, corresponding isomerides actually exist; for example, a 7- and a 9-methylpurine are both known, and similar examples occur frequently, and are always possible, so long as the imidazole ring contains no oxygen. Purine itself is only known in one form; in this and similar cases, where there is no reason to adopt one formula rather than another, formulæ are used corresponding with the first of those given above. For uric acid (trioxypurine), the formula of Medicus has been shown to be most suitable. The tautomeric enolic form would better exhibit the relations of uric acid to the chlorine and ethoxy-derivatives, but the author prefers the old ketonic formula for uric acid itself. For its sulphur analogue (trithiopurine), on the other hand, he prefers the tautomeric formula:

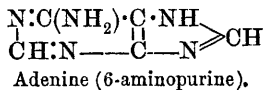
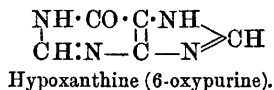
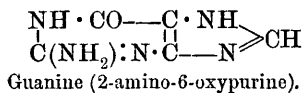
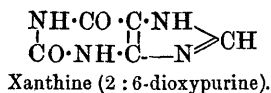


Uric acid (trioxypurine).



Trithiopurine.

These principles are applied throughout in the assignment of formulæ. Of these formulæ, the four next given are of special interest:



The methods used in synthesising members of the purine group are described as five in number :

(1) The preparation of uric acid from pseudo-uric acid,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , and of its alkyl derivatives by an analogous reaction. This conversion is usually effected by boiling with dilute hydrochloric acid (Abstr., 1897, i, 268); in the case of  $\psi$ -uric acid itself, a great deal of the solvent is necessary, but in the case of its methyl derivatives, this difficulty disappears, and the 1 : 3 : 7-trimethyl derivative is even converted by boiling with water alone.

(2) The methylation of oxypurines. This is best effected by shaking an alkaline solution of the oxypurine with methylic iodide either in the cold or at higher temperatures, for example, 80—90° (this vol., i, 392). In the case of uric acid, 3- and 9-methyl-, 3 : 9-, 1 : 3-, and 7 : 9-dimethyl-, 3 : 7 : 9-trimethyl-, and tetramethyl-uric acids are formed successively.

(3) The conversion of oxypurines into chloropurines by heating them with a mixture of phosphorus oxychloride and pentachloride (Abstr., 1884, 996), or with the oxychloride alone (this vol., i, 175, 176), at temperatures between 130° and 170°, the reaction being facilitated by shaking. The product formed is determined to a large extent by the conditions of the experiment; 2 : 6 : 8-trioxy-3 : 7-dimethylpurine (dimethyluric acid), for instance, yields 8-chloro-2 : 6-dioxy-3 : 7-dimethylpurine (chlorodimethylxanthine) when heated with phosphorus oxychloride, whilst with a mixture of oxychloride and pentachloride at 140° it yields 6-chloro-2 : 6-dioxy-3 : 7-dimethylpurine, and with excess of pentachloride at 170°, 2 : 6 : 8-trichloro-7-methylpurine, one methyl group being eliminated.

(4) Conversion of the halogen purines into oxy-, thio-, and amidopurines. The conversion into oxypurines can be effected by heating with aqueous alkali (Abstr., 1897, i, 642); but if a partial breakdown of the purine nucleus occurs, alcoholic potash may be used with advantage; this reacts at a comparatively low temperature, and produces alkoxy-derivatives (Abstr., 1897, i, 642). Concentrated hydrochloric acid at 125—130° is an even more efficient agent (Abstr., 1896, i, 14); an 8-chlorine atom is often removed most readily; sometimes, however, it remains persistently (Abstr., 1898, i, 180), whereas chlorine in another position is readily removed (this vol., i, 392). Aqueous potassium hydrosulphide effects the conversion of halogen into thio-derivatives with comparative readiness (Abstr., 1898, i, 340); the temperature employed was usually 100°, occasionally 120°. Alcoholic ammonia, at temperatures up to 150°,

effects the replacement of the halogen by the amido-group; no breaking down of the purine nucleus takes place in this case, and it is only small in amount when aqueous ammonia, which reacts rather more vigorously, is used. Diamido- but not triamido-derivatives can be prepared in this way, and by the action of nitrous acid a ready conversion into oxy-derivatives can often be effected.

(5) Reduction of the halogen purines, often by means of fuming hydriodic acid and phosphonium iodide (Abstr., 1884, 996). When no oxygen is present in the molecule, the yield is poor, however, and in this case it is better to treat with concentrated hydriodic acid at  $0^{\circ}$ , when, as a rule, some halogen is replaced by hydrogen, but some at the same time by iodine, and then to boil the resulting iodo-compound with zinc dust and water, when the iodine is replaced by hydrogen; in this way, 2:6:8-trichloropurine can be converted successively into 2:6-di-iodopurine and purine itself (this vol., i, 175). Boiling with zinc dust and water, to which a little ammonia may sometimes be added with advantage, also effects a partial replacement of chlorine by hydrogen; 2:6:8-trichloro-9-methylpurine yields 2-chloro-9-methylpurine, and 2:6:8-trichloro-7-methylpurine and 2:6-dichloro-7-methylpurine yield 2-chloro-7-methylpurine (this vol., i, 175).

There follows next a recapitulation of the more important purine derivatives, with their methods of preparation and properties.

After this, a number of decompositions of these purine compounds, observed for the first time by the author and his collaborators, and involving a breaking down of the purine nucleus, are enumerated; but first three decompositions, long known, are mentioned as of particular utility in determining the constitution of purine derivatives: (1) the formation of alloxan, recognised by the murexide test; heating with nitric acid effects this only in the case of the uric acids, amidodioxypurines and some halogen-xanthines, and then only with difficulty in some cases; aqua regia effects it in the case of xanthines, and some thio-derivatives; 2:8- and 6:8-dioxypurines; the monoxypurines, the oxydichloropurines, and all derivatives which contain a CH-group in the alloxan nucleus fail to give the reaction; (2) the formation of sarcosine, on heating with strong hydrochloric acid at  $170-200^{\circ}$ , which proves the presence of a 7-methyl group; (3) the formation of guanidine or a methylguanidine, recognised by means of their picrates, on treatment with hydrochloric acid and potassium chlorate; this did not happen in the case of 8-amino-2:6-dioxy-7-methylpurine, although it might have been expected to take place.

As regards the influence of constitution on properties, it is found that the introduction of oxygen, sulphur, or the amido-group lessens the solubility in water and raises the melting point. The introduction of methyl groups increases the solubility, volatility, and power of crystallising, and lowers the melting point. The oxidisability by nitric acid, or by chlorine and water, increases with the number of oxygen atoms or amido-groups present; it is sometimes lessened by the presence of methyl groups. The oxidisability by ammoniacal silver solution is also lessened by methyl, especially in the 7-position. The conversion of a  $\psi$ -uric into a uric acid is facilitated by the presence

of methyl, especially in the 7-position. The action of the chlorides of phosphorus varies considerably with the number of methyl groups present; and the breaking down of the purine nucleus by alkalis, as well as the elimination of halogens by aqueous or alcoholic alkali, is most readily effected in the case of those derivatives in which all the acid hydrogen has been replaced by methyl.

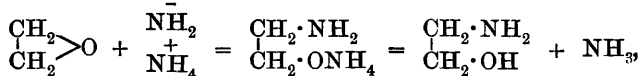
Finally, a list is given of all the compounds prepared by the author and his collaborators, together with a few that occur naturally, or have been prepared by other investigators. C. F. B.

**Influence of Water on the Addition of Ethylenic Oxide to Ammonia and Amines.** By LUDWIG KNORR (*Ber.*, 1899, 32, 729—732).—Acetalamine which has been dried over barium oxide does not react with ethylene oxide at the ordinary temperature, but in presence of water (1 mol.), complete combination occurs; the product, on distillation, gives off water, and on repeated fractionation yields a substance boiling at 253—255° under atmospheric pressure, which is probably 5-ethoxymorpholine,  $\text{NH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OEt}) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{O}$ . When methylacetalamine is used, the behaviour is similar, and the product finally obtained is doubtless 1-methyl-3-ethoxymorpholine,  $\text{NMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OEt}) \\ \text{CH}_2 \text{---} \text{CH}_2 \end{smallmatrix} \text{O}$ .

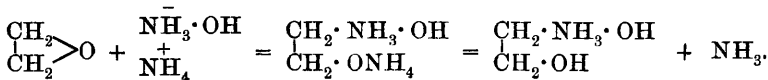
Ammonia, methylamine, and ethylamine, which, as a rule, act violently on ethylenic oxide, react with it only very slowly when quite dry, or not at all. Dry di-isobutylamine does not attack it at 85°, but in presence of water, combination occurs at the ordinary temperature. With diamylamine, interaction does not occur at 85°, but at 150° hydroxydiamylamidoethylic alcohol is formed.

The interaction of ammonia and ethylenic oxide is not due to the addition to the latter of  $\text{NH}_4^+$  and  $\text{OH}^-$ , which are usually assumed to be the ions present in an aqueous solution of ammonia, but apparently to the addition of  $\text{H}^+$  and  $\text{NH}_2^-$  or of  $\text{H}^+$  and  $\text{NH}_3 \cdot \text{OH}^-$ . The concentration of the hydrogen ions in a solution of ammonia, however, cannot be greater than in water, owing to the presence of  $\text{OH}^-$  ions, hence it must be supposed that the ion  $\text{NH}_2^-$  or  $\text{NH}_3 \cdot \text{OH}^-$  is present in the solution in addition to  $\text{OH}^-$  and  $\text{NH}_4^+$ .

With this assumption, the behaviour of ethylenic oxide in a solution of ammonia may be explained by one of the following equations:



or



A. L.

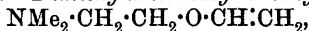
**Breaking-down of Phenomorpholine by Exhaustive Methylation.** By LUDWIG KNORR (*Ber.*, 1899, 32, 732—736).—Griess observed that the methylhydroxide of orthodimethylamidoanisole, when heated, breaks down into methylic alcohol and dimethylanisidine (Abstr., 1880, 638), and in similar manner, as shown by Königs and Feer (Abstr., 1885, 1245), dimethyltetrahydroquinolium hydroxide yields kairoline at 150°. The authors find that a similar decomposition occurs when dimethylphenomorpholinium iodide is heated with strong soda, the product obtained being dimethylorthamidophenyl vinyl ether.

*Dimethylphenomorpholinium iodide*,  $C_{10}H_{14}NOI$ , separates in the form of hard prisms when a mixture of equal parts of methylphenomorpholine, methylic alcohol, and methylic iodide is left overnight; it decomposes indefinitely at 200°.

*Dimethylorthamidophenyl vinyl ether*,  $C_{10}H_{13}NO$ , forms a mobile, colourless oil having a pungent odour and neutral reaction; it is scarcely soluble in water, dissolves readily in the usual organic solvents, and boils at 224—225°. It behaves towards litmus, gold chloride, ammoniacal silver nitrate, ferric chloride, diazobenzene chloride, and nitrous acid in much the same manner as does methylphenomorpholine. The *methiodide*,  $C_{11}H_{16}NOI$ , crystallises in rounded aggregates; the *picrolonate*,  $C_{10}H_{13}NO, C_{10}H_8N_4O_5$ , crystallises in slender needles when its hot alcoholic solution is slowly cooled, and melts at 145—146°. The *picrolonate* of *methylphenomorpholine*,  $C_{19}H_{19}N_5O_6$ , separates from hot alcohol as a heavy, crystalline, sandy powder, and melts at 164—165°.

A. L.

**Breaking-down of the Morpholine Ring by Exhaustive Methylation.** By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1899, 32, 736—742).—*Dimethylamidoethylic vinyl ether*,

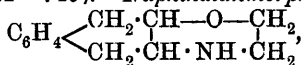


is made by acting on methylmorpholine methiodide in concentrated aqueous solution with freshly precipitated silver oxide and subjecting the product to fractional distillation. Aldehyde is at first observed as a decomposition product, but the amount produced gradually decreases, and finally a concentrated, strongly alkaline solution of the vinyl ether distils over, from which the ether may be isolated by extraction with ethylic ether and distillation over caustic soda. It forms a colourless, mobile liquid having an odour resembling that of dimethylethanolamine [dimethylamidoethylic alcohol] and methylmorpholine; it boils at 124° under 740 mm. pressure, is miscible in all proportions with water, alcohol, and ether, is very volatile, and distils readily in steam or ether vapour. Its aqueous solution gives precipitates with many alkaloidal reagents. The *picrate*,  $C_6H_{13}NO, C_6H_2N_3O_7$ , crystallises in light yellow, orthorhombic tablets, melts at 85°, and dissolves readily in water and alcohol. The *picrolonate*  $C_6H_{13}NO, C_{10}H_8N_4O_5$ , crystallises from hot dilute alcohol in small, shining, brownish-yellow cubes, dissolves somewhat sparingly in water but readily in alcohol, and melts and decomposes at 138°. The *hydrochloride* is hygroscopic, but may be obtained in long, compact needles; the *aurichloride*,



$C_6H_{13}NO$ ,  $HAuCl_4$ , crystallises from hot water in delicate, bright yellow, sparingly soluble needles; the *platinochloride*,  $(C_6H_{13}NO)_2 \cdot H_2PtCl_6$ , is readily soluble in water, and separates on addition of alcohol to its aqueous solution as a pale yellow precipitate; the *methiodide* of dimethylamidoethylic vinylic ether,  $NMe_3I \cdot CH_2 \cdot CH_2 \cdot O \cdot CH : CH_2$ , crystallises from a mixture of ether and methylic alcohol in small, compact crystals which are octahedra or combinations of octahedra and rhombic dodecahedra. When it is heated in aqueous solution with moist silver oxide and the product submitted to distillation, a polymeride of divinyl ether is deposited, and a mixture of trimethylamine and acetylene is given off, together with a substance, possibly divinyl ether, which may be obtained on neutralising the distillate with hydrochloric acid and distilling once more; the supposed divinyl ether forms a mobile liquid which burns with a blue, non-luminous flame and forms an explosive mixture with air. A. L.

**Decomposition of Naphthalanmorpholine by Exhaustive Methylation: Constitution of Morphine.** By LUDWIG KNORR, (*Ber.*, 1899, 32, 742—749).—*Naphthalanmorpholine*,

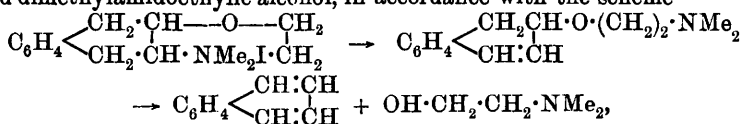


may be obtained from tetrahydronaphthalene oxide by uniting it with amidoethylic alcohol, and treating the resulting *hydroxyethylamido-tetrahydro-β-naphthol* with condensing agents. Its constitution is analogous to that of morphine, which the author (*Abstr.*, 1889, 905)

represents by the formula,  $OH \cdot C_{10}H_{13} \begin{cases} CH(OH) \cdot CH - O - CH_2 \\ CH_2 - CH \cdot NMe \cdot CH_2 \end{cases}$ .

Naphthalanmorpholine is a strong, alkaloid-like, stable base which is not altered by distillation under atmospheric pressure, has a neutral reaction, yields well-crystallised salts, and is precipitated from very dilute solution by most alkaloidal reagents. Its N-alkyl derivatives are very active physiologically, and closely resemble morphine in their effect on the human system.

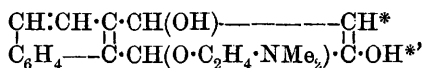
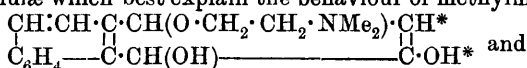
Naphthalanmorpholine may be converted into the *methiodide* of *methylnaphthalanmorpholine*, which is readily converted into *dihydro-β-naphthyllic dimethylamidoethylic ether*, and the latter into naphthalene and dimethylamidoethylic alcohol, in accordance with the scheme



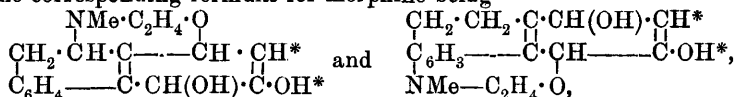
a decomposition exactly analogous to that of codeine into methylmorphomethine, and finally into methyl-dihydroxyphenanthrene and dimethylamidoethylic alcohol. A remarkable point of difference, however, is found in the extraordinary readiness with which dihydro-β-naphthyl ether undergoes the secondary change, it being merely necessary to treat the aqueous solution of the substance with 1 per cent. hydrochloric acid in order to effect an immediate separation of naphthalene. This fact supplies an explanation of many changes which have been observed in the study of certain alkaloids, and

illustrates the great readiness shown by many dihydrogenised benzenoid compounds to revert to true aromatic systems. Thus the production of thebenine and morphothebaine from thebaine by the action of dilute or strong hydrochloric acid is probably due to the presence of the morpholine group in attachment to a dihydrogenised nucleus. The relatively great difficulty observed in breaking up methylmorphomethine into hydramine and a phenanthrene derivative would therefore appear to exclude the supposition that methylmorphomethine is a derivative of orthodihydrophenanthrene.

As methylmorphomethine contains three asymmetric carbon atoms, which can only be explained on the supposition that they exist as  $>\text{CH}\cdot\text{OH}$  or  $>\text{CH}\cdot\text{O}(\text{CH}_2)_2\cdot\text{NMe}_2$ , it must be assumed that the substance is a paradihydrophenanthrene derivative; moreover, as Vongerichten has recently shown that morphol yields phthalic acid on oxidation (this vol., i, 307), the methoxy-group of methylmorphomethine is attached to the dihydrogenised benzene nucleus. The formulæ which best explain the behaviour of methylmorphomethine are



the corresponding formulæ for morphine being



the ethanoldimethylamine residue being attached to two carbon atoms in the peri-position, and not in an ortho-position, as has hitherto been assumed. Of these two formulæ for morphine, the author prefers the former, which bears a striking resemblance to that proposed for papaverine by Goldschmidt.

The dihydro- $\beta$ -naphthylidic dimethylamidoethylic ether is made by boiling methyl-naphthalanmorpholine methiodide with 10 per cent. soda whilst steam is passed through the hot liquid; it is extracted from the distillate by cooling, separating the naphthalene by filtration, and extracting the filtrate with ether. It forms a somewhat mobile oil, is alkaline to moist litmus, and forms a *methiodide* which crystallises in rounded aggregates and decomposes at  $140^\circ$ . It dissolves readily in most of the usual organic media, but is only sparingly soluble in water. In very dilute aqueous solution, it does not yield precipitates with alkaloidal reagents. When the substance is warmed with strong soda, it breaks up gradually into naphthalene and hydramine, and the same decomposition is effected quantitatively in a few moments by mineral acids, and goes on more slowly when organic acids are used.

A. L.

**Cevadine [Veratrine].** By MARTIN FREUND and HEINRICH P. SCHWARZ (*Ber.*, 1899, 32, 800—806).—Commercial cevadine [veratrine], when recrystallised from alcohol, does not melt at  $205^\circ$  as stated by E.

\* There is at present no evidence as to which of these positions is occupied by the OH-group.

Schmidt (Abstr., 1878, 516), but softens at  $110^{\circ}$  and gradually passes into a transparent resin; this is due to the fact that the alkaloid combines with alcohol of crystallisation, which is lost either on drying at  $130$ — $140^{\circ}$  or on boiling with water, the pure substance then melting at  $205^{\circ}$ .

On treatment with alcoholic potassium hydroxide, veratrine is resolved into a base cevine (Wright and Luff, Trans., 1878, 33, 323) and a mixture of angelic and tiglic acids. Cevine,  $C_{27}H_{43}NO_8 + 3\frac{1}{2}H_2O$ , separates from water containing a little alcohol in well formed crystals belonging to the triclinic system; the water of crystallisation is given off at  $105$ — $110^{\circ}$ , and the anhydrous substance softens at  $155$ — $160^{\circ}$ , becomes a transparent resin at  $165$ — $170^{\circ}$ , and melts at  $195$ — $200^{\circ}$ . It reduces ammoniacal silver nitrate and Fehling's solution. On treatment with alcoholic potassium hydroxide, it yields the *potassium* compound, crystallising in slender needles which darken at  $240^{\circ}$  and decompose at  $246^{\circ}$ ; the *sodium* compound, prepared by treating the base with strong aqueous sodium hydroxide, decomposes at  $260$ — $265^{\circ}$ ; the *hydrochloride* forms beautiful needles melting at  $240^{\circ}$ ; the *methiodide* separates from its alcoholic solution on addition of ether in crystals melting at  $240$ — $250^{\circ}$ .

The paper concludes with a description of the physiological properties of veratrine and cevine. J. F. T.

**Reducing Substances obtained from Egg-albumin.** By JOHN SEEMANN (*Chem. Centr.*, 1898, ii, 1271; from *Diss. Marburg*).—The carbohydrate substance (compare Müller, *Sitz-Ber. ges. Naturw. Marburg*, 1898, 117) is isolated from white of egg, by treating 25 grams of the substance, free from ovomucoid, with 400 c.c. of very dilute alkali, and then adding 100 c.c. of hydrochloric acid of a concentration such that the mixture shall contain 2—3 per cent. of the acid. After passing steam through the hot liquid, titration with Fehling's solution showed a content of 9 per cent. of a reducing substance calculated as dextrose; from ovomucoid, 30.9 per cent. was obtained. This substance was identified as glucosamine (chitosamine).

E. W. W.

**Formation of Sugar from Albumin.** By FERDINAND BLUMENTHAL (*Compt. rend.*, 1899, 128, 117—120).—When egg-albumin is dissolved in water, mixed with sodium or barium hydroxide solution, and after an hour or two is acidified with hydrochloric acid, boiled, neutralised with sodium hydroxide, re-acidified with acetic acid, evaporated to dryness, and extracted with hot alcohol of 93 per cent., it yields a hexose which has the general properties of a glucose, and after removal of albumoses and peptones, is slightly lævogyrate, even after allowing for the possible presence of small quantities of albumoses. It is not fermented by beer-yeast, and hence would seem to be levulose; the quantity obtained amounts to from 8 to 12 per cent. of the albumin. C. H. B.

**Formation of Sugar from Albumin.** By FERDINAND BLUMENTHAL and PAUL MAYER (*Ber.*, 1899, 32, 274—278).—When purified white of egg is boiled with dilute hydrochloric acid, a liquid is

obtained which yields an osazone having the composition of glucosazone; this melts at 200—205°, but is not levorotatory in acetic acid solution. Similar results are obtained with the albumin from the yolk of egg after extracting the fat with ether and washing with water and alcohol; the osazone obtained in this case melts at 203°, and is levorotatory in acetic acid solution. Both osazones appear to be somewhat impure glucosazone. It seems probable that the separation of the carbohydrate is not accompanied by destruction of the albumin molecule, and that the residue still belongs to the class of albumins.

A. H.

**Crystallised Fibrin.** By A. MAILLARD (*Compt. rend.*, 1899, 128, 373—375).—Some tubes of antidiabetic serum several months old were found to contain a deposit of fibrin in small, angular crystals which acted on polarised light and seemed to belong to the monoclinic system. These crystals gave all the ordinary reactions of fibrin. Similar crystals were obtained from ordinary ox serum, and the author adopts the view that whether fibrin is crystalline or amorphous depends mainly on the rate at which it separates from the liquid in which it is formed.

C. H. B.

**Proteid of Wheat-gluten.** By KURATA MORISHIMA (*Chem. Centr.*, 1898, ii, 1102; from *Arch. exp. Path. Pharm.*, 41, 345—354).—According to the author, wheat-gluten contains only one proteid, *artolin*, which is prepared by extracting with dilute alkali, precipitating with dilute acid, and purifying by dissolving it in water or dilute alcohol, and precipitating with absolute alcohol and ether. From concordant analyses of several preparations, the formula  $C_{185}H_{288}N_{50}SO_{68} \cdot 2HCl$  is ascribed to the hydrochloride. Artolin is slightly soluble in cold, but more easily soluble in hot, water, and the hot solution, on cooling, becomes turbid; it is easily soluble in very dilute mineral acids, in alkalis, in a large volume of acetic acid, and in moderately dilute alcohol; it is precipitated from its alcoholic solution by adding a large quantity of absolute alcohol or of water.

The portion of the gluten which is insoluble in dilute alkali is very rich in phosphorus.

E. W. W.

**The Proteid-like Substances of Silk.** By G. WETZEL (*Zeit. physiol. Chem.*, 1899, 26, 535—542).—Fibroin, silk-gelatin, and conchiolin yield, with acids, basic materials similar to the protamines. In the case of fibroin, the yield is a small one.

W. D. H.

**Glutolin, a Proteid of Blood-serum.** By EDWIN S. FAUST (*Chem. Centr.*, 1898, ii, 1105; from *Arch. exp. Path. Pharm.*, 41, 309—324).—Glutolin,  $C_{204}H_{336}N_{60}SO_{70}$ , is obtained by adding an equal volume of a saturated solution of ammonium sulphate to the serum of horse blood, dissolving the precipitate in a large quantity of water, making the solution feebly acid with acetic or hydrochloric acid, and then saturating the solution with carbonic anhydride. The precipitate, which is generally plastic like dough, is kneaded with a 10 per cent. solution of sodium chloride, and then treated with a 0.5 per cent. solution of potassium hydroxide. The filtrate, when neutralised with hydrochloric acid, yields a flocculent precipitate of

glutolin which does not contain serum-globulin, for it does not turn alkaline lead solutions black on boiling; it is insoluble in solutions of neutral salts, soluble in alkali hydroxides and ammonia, gives the biuret reaction in the cold, and Millon's reaction faintly. Glutolin belongs to the glutins, and like glutin, when decomposed with hydrochloric acid, yields glycocine, which was identified by converting it into hippuric acid; the other proteids of blood do not give this reaction. The author regards glutolin as a compound intermediate in composition between albumin and glutin, and as the parent substance from which the glutinous portion of the tissue is derived.

E. W. W.

**Nucleins.** By ALBERT NEUMANN (*Chem. Centr.*, 1898, ii, 1211; from *Arch. Anat. Phys.*, 1898, 374—378).—According to the author, nucleic acid consists of three acids, *a*- and *b*-nucleic acids and nucleothymic acid. The *a*- differs from the *b*-nucleic acid in that 5 per cent. solutions of its salts gelatinise, whilst those of the *b*-acid do not. Nucleothymic acid, which is a nuclein, since it contains phosphorus, carbohydrates, and alloxuric bases, is also formed by hydrolysing *a*- or *b*-nucleic acid, and, unlike thymic acid, is precipitated by hydrochloric acid. The alloxuric bases formed by decomposing *a*- and *b*-nucleic acids give the xanthine reaction with nitric acid and sodium hydroxide solution, whilst those obtained from nucleothymic acid do not give this reaction. All three acids give Tollens' pentose reaction with phloroglucinol and hydrochloric acid. In order to test for nucleins, acetic acid is added to the cold solution, whereby the nucleins containing albumin are precipitated; the nucleins which do not contain albumin are then thrown down by hydrochloric acid, and the acid mixture boiled until the precipitate is dissolved. The solution gives a cherry-red coloration with phloroglucinol and concentrated hydrochloric acid, and when warmed with an excess of ammonia and silver nitrate, forms a flocculent precipitate of alloxuric silver compounds. The phosphoric acid in nucleins is determined by treating the ash with sodium carbonate and nitric acid. The three nucleic acids are easily dissolved, but not attacked by the alkaline digestive juices. When administered to a dog, four-fifths are eliminated in the urine, and one-fifth in the fæces. Nucleic acid, when administered per os, or nucleothymic acid when subcutaneously injected, in a few hours causes strong hyperleucocytose which is not preceded by hypoleucocytose, but the sodium salts of these acids do not produce this result, the author experiencing no effects from a dose of 10 grams.

E. W. W.

**Action of Hydrogen Sulphide and Acids on Blood-pigment.** By ERICH HARNACK (*Zeit. physiol. Chem.*, 1899, 23, 558—585).—Hæmoglobin free from oxygen is not affected by hydrogen sulphide alone, but it is if previously saturated with carbonic anhydride. The new substance formed is of a dark-red colour, and shows a characteristic absorption band in the orange; it is termed sulph-hæmoglobin, and is considered to be a compound of the pigment with hydrogen sulphide. By dilute acid, it is broken up into hydrogen sulphide and acid-hæmoglobin.

W. D. H.

**Colouring-matters of Blood and Bile.** By WILLIAM KÜSTER (*Ber.*, 1899, 32, 677—682).—Dibasic hæmatic acid,  $C_8H_{10}O_2$ , was stated to be obtained by oxidising hæmatin (*Abstr.*, 1896, i, 516) or hæmatoporphyrin (*Abstr.*, 1897, i, 232) with sodium dichromate in acetic acid solution. It is now shown that the same product is obtained, whether the source of the hæmatin be the blood of oxen, horses, or sheep, but that it contains nitrogen, and is identical with the biliverdic acid,  $C_8H_9NO_4$ , obtained by the oxidation of the bilirubin of gall-stones (*Abstr.*, 1897, i, 647). When warmed with sodium hydroxide solution, it loses ammonia, and yields the anhydride of tribasic hæmatic acid,  $C_8H_8O_5$ , an exchange of the NH-group for oxygen taking place. *Calcium biliverdate*,  $(C_8H_8NO_4)_2Ca + H_2O$ , is obtained by treating an aqueous solution of the acid with calcium carbonate at the ordinary temperature, and leaving the solution to evaporate spontaneously; as the anhydride,  $C_8H_8O_5$ , may be formed to some extent, it is better to extract the solution with ether before evaporating it, otherwise the calcium salt crystallises with difficulty. It is just possible that this acid is a mixture of isomerides.

The anhydride of tribasic hæmatic acid melts at  $97-98^\circ$  when pure; the corresponding *silver* salt has the composition  $C_8H_7Ag_3O_6 + \frac{1}{2}H_2O$ ; by treatment with cold water and calcium carbonate, a solution is obtained from which a basic calcium salt is precipitated when heat is applied. When reduced with hydriodic acid, it yields a tribasic *acid*,  $C_8H_{12}O_6$ , which is stable towards permanganate; possibly this is a mixture of isomerides.

C. F. B.

**Formation of Melanin-like Pigments from Proteids.** By RUSSELL H. CHITTENDEN and ALICE H. ALBRO (*Amer. J. Physiol.*, 1899, 2, 291—305).—The possibility of the relationship of the melanins to anti-albumid was first pointed out by Schmiedeberg on account principally of the high percentage of carbon in both. In the present research, the hydrolytic cleavage of anti-albumid produced by prolonged boiling with sulphuric acid gave rise to a black pigment with a higher percentage of carbon than in the original substance; this pigment is soluble in alkalis and can be precipitated by acetic acid. Hemipeptone, treated in the same way, yields a similar pigment, with a different percentage composition. The artificial melanins resemble, therefore, the natural ones in being numerous.

W. D. H.

## Organic Chemistry.

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**The Negative Nature of Unsaturated Groups of Atoms.** By FERDINAND HENRICH (*Ber.*, 1899, 32, 668—676. Compare *Abstr.*, 1898, i, 631).—The ethylene group,  $\cdot\text{CH}:\text{CH}\cdot$ , appears to be negative in character; that is to say, it confers replaceability on the hydrogen atoms of a  $\text{CH}_2$ -group when this radicle is attached to it as well as to a CO-group. These hydrogen atoms in diethylic glutaconate,  $\text{COOEt}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOEt}$ , can be replaced successively by methyl, by dissolving the substance in alcoholic sodium ethoxide and adding methylic iodide to the solution. *Dimethylglutaconic acid* melts at  $129\text{--}130^\circ$ , and undoubtedly has both the methyl groups attached to the same carbon atom, since it is oxidised by permanganate to dimethylmalonic acid, and does not react with nitrous acid. Further, ethylic glutaconate condenses with diazobenzene chloride, with benzaldehyde and sodium ethoxide, and also with acetaldehyde in the presence of diethylamine.

It is pointed out that the acetylene group,  $\cdot\text{C}:\text{C}\cdot$ , is more strongly negative than the ethylene group,  $\cdot\text{CH}:\text{CH}\cdot$ ; further, that the group  $\cdot\text{CH}:\text{N}\cdot$  is also negative, possibly more so than  $\cdot\text{CH}:\text{CH}\cdot$ ; and that  $\cdot\text{C}:\text{N}$  is certainly more negative than  $\cdot\text{C}:\text{C}\cdot$ . The azo-group  $\cdot\text{N}:\text{N}\cdot$  is negative in amidoazobenzene and its dinitro-derivative; still more so in azoimide. In all these radicles, and in the ordinary negative groups  $\cdot\text{CHO}$ ,  $\cdot\text{COOEt}$ ,  $\cdot\text{CRO}$ ,  $\cdot\text{CO}\cdot\text{CO}\cdot\text{COOEt}$ , &c., atoms of like or unlike kinds occur linked together by double or triple bonds, and the author concludes that "a negative radicle thus appears to be characterised by—indeed its negative character appears to be a consequence of—the occurrence in the radicle of like or unlike atoms in intimate union, that is, doubly or triply linked to each other." C. F. B.

**Electronegative Character of certain Unsaturated Organic Radicles.** By ERNEST CHARON (*Compt. rend.*, 1899, 128, 736—739).—The author regards the group  $\text{R}\cdot\text{CH}:\text{CH}\cdot$  as a radicle having well marked electronegative characters, and bases this opinion on (1) the formation of a large proportion of pinacone by the reduction of crotonaldehyde, the quantity of pinacone found in such reactions being greater the more pronounced the electronegative character of the molecule; (2) the ready formation of crotonylic bromide, chloride, and iodide by action of the halogen hydracids on crotonylic alcohol; (3) the unstability of crotonylic iodide when exposed to light, as compared with the stability of allylic iodide. Henrich's observation, that in phenylic ethylic glutaconate,  $\text{COOPh}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{COOEt}$ , both hydrogen atoms of the  $\text{CH}_2$ -group are readily replaced by an alkylic group, affords further confirmation of this view. C. H. B.

**Action of Zinc Dust on Dibromides,  $\text{C}_n\text{H}_{2n}\text{Br}_2$ , in Alcoholic Solution.** By WLADIMIR IPATIEFF (*Chem. Centr.*, 1898, ii, 472; from *J. Russ. Chem. Soc.*, 1898, 30, 292—297).—By the action of zinc dust on dibromides in which the bromine atoms are not united to con-

tiguous carbon atoms, closed chain hydrocarbons are obtained, whilst with those containing the bromine united to adjacent carbon atoms, olefines are formed. By the action of zinc dust on dibromo- $\beta$ -dimethylethylene, prepared from dimethylallene (*J. Russ. Chem. Soc.*, 27, 387), however, a hydrocarbon which boils at 35—38° and has a composition corresponding with that of trimethylethylene, is formed. This substance combines with bromine forming dibromotrimethylethylene, from which, by the action of alcoholic potassium hydroxide, an unsaturated compound,  $C_5H_8Br$ , is obtained. Dibromotrimethylethane, prepared from bromine and dimethylethylcarbinol (*J. Russ. Chem. Soc.*, 27, 374), when treated with zinc dust, yields trimethylethylene, from which dibromisopropylethane,  $CHMe_2 \cdot CHBr \cdot CH_2Br$ , is obtained by the action of bromine; the latter is also prepared by the action of bromine on isopropylethylene (*J. Russ. Chem. Soc.*, 1877, 151) boils at 64—66°, has a sp. gr. 1.7162 at 0°, and when treated in alcoholic solution with zinc dust yields pure isopropylethylene. E. W. W.

**Action of Bromine on Ethylic Bromide in Presence of Aluminium Bromide.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 497—499).—A detailed account of work already published (compare this vol., i, 1). G. T. M.

**Action of Aluminium Chloride on Acetylene Tetrachloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 499—500).—When acetylene tetrachloride is heated to 110° in the presence of aluminium chloride, hydrogen chloride is evolved, carbon deposited, and a certain quantity of the isomeric unsymmetrical tetrachlorethane produced; dichloroacetylene could not be detected, and the deposition of carbon is probably due to the decomposition of this substance. G. T. M.

**Action of Bromine on Acetylene Tetrachloride in Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, 19, [iii], 500—502).—Contains details of a reaction previously studied (compare Abstr., 1898, i, 614). G. T. M.

**Thio-derivatives obtained by the Action of Aluminium Haloids on Organic Compounds. Synthesis of Thiocarbonates.** By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1898, ii, 361—362; from *J. Russ. Chem. Soc.*, 1898, 30, 12—22).—When a solution of aluminium bromide in carbon bisulphide is mixed with ethylenic bromide in a closed tube, the mixture becomes turbid in 10—30 minutes, a heavy, brown oil separates, and after a time forms a crystalline mass. The reaction takes place without development of heat or liberation of gas. The liquid portion is separated, and the crystals of the compound,  $AlBr_3 \cdot C_2H_4Br_2 \cdot CS_2$ , are washed with ethylenic bromide and dried at 50—60° in a stream of carbonic anhydride; they fume in the air, becoming opaque, and, when heated, are not affected below 120°, but melt and decompose at 137—138°. This compound is almost insoluble in organic solvents, and very slightly soluble in acetic chloride; it reacts energetically with water, forming ethylenic dithiocarbonate,  $CO \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ S \end{smallmatrix} C_2H_4$ , melting at 33—34° (Gusemann gave 31°),



and, with alcoholic ammonia, yielding thioethylenic glycol and carbamide.

When a solution of aluminium bromide in carbon bisulphide is treated with ethylic bromide, the compound  $(\text{AlBr}_3, \text{EtBr})_2, \text{CS}_2$  separates after 7 days as a heavy oil, which, by the action of water, yields diethylic dithiocarbonate,  $\text{CO}(\text{SEt})_2$ .

Propylic bromide, bromoform, propylenic bromide, and tribromopropane react with aluminium bromide and carbon bisulphide in a similar manner, and with amylenic bromide there is a violent reaction, with liberation of hydrogen bromide.

Carbon bisulphide combines, but much more slowly, with aluminium chloride and ethylenic chloride, and also with aluminium iodide and methylic or ethylic iodide.

E. W. W.

**Synthesis of Ethylic Alcohol.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 862—864).—It has been stated that alcohol was first synthesised from ethylene by Hennell in 1828; this, however, is not the case. From sulphuric acid which had absorbed ethylene, Hennell simply obtained a potassium salt which resembled the potassium ethylic sulphate obtained by him from alcohol; no analysis of the salt was given, however, nor was alcohol regenerated from it. The author first effected this synthesis, and showed that the alcohol obtained from pure ethylene and sulphuric acid had the same properties as ethylic alcohol produced by fermentation (compare this vol., i, 182).

G. T. M.

**Manufacture of Ethylic Alcohol from Sawdust.** By E. SIMONSEN (*Bied.-Centr.*, 1899, 28, 200—202; from *Festschr. tech. Schule Christiania*, 1898, 22. Compare Abstr., 1896, i, 331).—Sawdust and dilute acid are heated in an autoclave of 1 cubic metre capacity under a pressure of 9 atmospheres. The fineness or otherwise of the sawdust has no appreciable effect, and probably shavings, cut short, would answer equally well for the production of alcohol. The amount of liquid must be four times that of the wood, and it should contain 0.5 per cent. of sulphuric acid.

The extracted wood is pressed (17.1 kilograms per square centimetre) and afterwards used for burning.

As regards the amount of sugar produced, the usual quantity is about 22 per cent. of the air-dried wood. The volume of the solution varies, but is greater than that of the liquid added to the wood; it contains about 5 per cent. of sugar. The acidity of the solution increases during the boiling; the acid produced is, in part, acetic acid. It is not found desirable to use the same acid for more than one quantity of wood. In fermentation, the liquid is nearly, but not quite, neutralised; the best temperature is 25°; more than 75 per cent. of the sugar, determined with Fehling's solution, remained unfermented.

The greatest yield of alcohol amounted to 7 litres from 100 kilograms of air-dried sawdust; the alcohol was of very good quality, and after being distilled over lime was as pure as rectified alcohol.

N. H. J. M.

**Action of Fermentation Amylic Alcohol on Sodium Amyloxide.** By GUERBET (*Compt. rend.*, 1899, 128, 511—513).—When

sodium is dissolved in boiling fermentation amylic alcohol, consisting chiefly of the inactive modification, the products, in addition to hydrogen and sodium amyloxide, are sodium isovalerate, diamylic alcohol,  $C_{10}H_{21}\cdot OH$ , the isovalerate derived from this alcohol, and a *divaleric acid*,  $C_{10}H_{20}O_2$ .

*Diamylic alcohol* boils at  $210-211^\circ$  (corr.), and does not freeze at  $-20^\circ$ , is a colourless liquid with a faint odour, dissolves in alcohol or ether, but is insoluble in water. Its *isovalerate* boils at  $173-175^\circ$  under 80 mm. pressure. *Divaleric acid*,  $C_{10}H_{20}O_2$ , is a colourless oil, insoluble in water, but soluble in alcohol and ether; it boils at  $164-165^\circ$  under 46 mm. pressure, and forms crystallisable sodium, calcium, and barium salts. In the reaction under consideration, it is produced from the alcohol by the action of sodium hydroxide,  $C_{10}H_{21}\cdot OH + NaOH = C_{10}H_{19}O_2Na + 2H_2$ , or by oxidation with chromic mixture.

The action of sodium amyloxide on amylic alcohol is represented by the equation  $C_5H_{11}\cdot ONa + C_5H_{11}\cdot OH = C_{10}H_{21}\cdot OH + NaOH$ , and the sodium hydroxide acts on some of the amylic alcohol and produces sodium isovalerate, and also acts on the higher alcohol in a similar manner. C. H. B.

**Action of Alcohols on their Sodium Derivatives.** By GUERBET (*Compt. rend.*, 1899, 128, 1002—1004).—*Diamylic alcohol* (preceding abstract) has a sp. gr. 0.8491 at  $0^\circ$ ; when heated with potassium hydrogen sulphate, it loses water and forms a liquid *decylene*,  $C_{10}H_{20}$ , of sp. gr. 0.7705 at  $0^\circ$ , boiling at  $155^\circ$ , and having an odour like turpentine. The *chloride*,  $C_{10}H_{21}Cl$ , obtained by the action of phosphorus pentachloride on the alcohol, is a colourless, oily liquid boiling at  $130-132^\circ$  under 70 mm. pressure; it cannot be distilled under ordinary pressure. *Diamylic acetate*, prepared by the action of acetic chloride on the alcohol, boils at  $132-133^\circ$  (corr.) under a pressure of 50 mm. and at  $218-220^\circ$  under atmospheric pressure, and has a sp. gr. 0.8701 at  $0^\circ$ . *Diamylic isovalerate* (*loc. cit.*) boils at  $258-259^\circ$  under atmospheric pressure. *Divaleric acid* (*loc. cit.*) is formed by the oxidation of diamylic alcohol with fused potash or chromic acid mixture; it is a colourless, oily liquid boiling at  $162-163^\circ$  and  $248-250^\circ$  under pressures of 50 and 760 mm. respectively. The *chloride*,  $C_{10}H_{19}ClO$ , boils at  $115^\circ$  under 60 mm. pressure, and the *amide*,  $C_{10}H_{21}NO$ , melts at  $112^\circ$ ; the latter dissolves readily in alcohol, and is sparingly soluble in water.

When ethylic alcohol is heated with sodium ethoxide in sealed tubes at  $210^\circ$ , the following reaction occurs:  $C_2H_6O + C_2H_5NaO = C_2H_4 + H_2 + CH_3\cdot COONa$ . Isobutylic alcohol, under these conditions, gives rise to a small quantity of sodium isobutyrate and another product boiling at  $115-150^\circ$ , which was not further characterised. G. T. M.

**Oxidation of Secondary and Tertiary Amines.** By WILLIAM CECHNER DE CONINCK (*Compt. rend.*, 1898, 128, 682—683. Compare this vol., i, 243 and 244).—Trimethylamine hydrochloride and pyridine are not affected by potassium dichromate and sulphuric acid. Dimethylamine hydrochloride and  $\alpha$ - and  $\beta$ -picolines are slightly oxidised, whilst  $\beta$ -lutidine,  $\alpha$ - and  $\beta$ -collidines, quinoline, and lepidine are readily

decomposed, especially on warming the mixture. Azobenzene, under similar conditions, yields carbonic anhydride and a trace of nitrogen.

G. T. M.

**Action of Nitrosyl Chloride on Fatty Amines.** I. Primary Monamines. II. Secondary Amines. By WASSILY A. SOLONINA (*Chem. Centr.*, 1898, ii, 887—888; from *J. Russ. Chem. Soc.*, 30, 431—449, 449—453).—(1) When a solution of nitrosyl chloride in ether is slowly added to an ethereal solution of benzylamine at  $-15$  to  $20^{\circ}$ , — benzylic chloride and benzylamine hydrochloride are formed. With isobutylamine, dissolved in metaxylene, under similar conditions, isobutylic chloride, with some tertiary butylic chloride and nitrosodi-isobutylamine, are formed, whilst pseudobutylamine yields pseudobutylic chloride, isoamylamine, and isoamylic chloride. Propylamine and ethylamine in ethereal solution yield propylic chloride and nitrosodiethylamine respectively, and from heptylamine, heptylic chloride and traces of heptylene are obtained. From the products of the reactions with allylamine and methylbutylallylcarbinamine, no definite compounds could be isolated.  $\alpha$ -Camphylamine gives a good yield of  $\alpha$ -camphylic chloride; this compound combines readily with bromine, and by the action of sodium phenoxide forms  $\alpha$ -camphylic phenylic ether,  $C_{10}H_{17}\cdot OPh$ , which is easily soluble in alcohol, ether, and benzene, has a characteristic odour, and boils at  $178$ — $180^{\circ}$  under 20 mm. pressure.

In the action of nitrosyl chloride on amines, the nitrous and hydrochloric acids resulting from the action of water on the chloride combine with the amines, and, probably, intermediate diazo-compounds are also formed. The formation of small quantities of isomerides was observed only in the cases of iso- and pseudo-butylamine.

(2) By the action of nitrosyl chloride on secondary amines, the hydrochlorides of the amines and nitrosamines are formed. In this way, nitrosodi-isobutylamine, nitrosodipropylamine, and nitrosodi-isoamylamine were obtained from the corresponding amines, and nitroso-piperidine from piperidine. The hydrochlorides of the amines were identified amongst the compounds obtained by means of benzenesulphonic chloride.

E. W. W.

**Constitutional Formula of Hexamethylenetetramine.** By GIUSEPPE GRASSI-CRISTALDI and A. MOTTA (*Gazzetta*, 1899, 29, i, 33—48).—The various constitutions which have been proposed for hexamethylenetetramine are discussed, and the conclusion drawn that the only one agreeing with all the known reactions is Lösekann's, namely,  $N(CH_2\cdot N:CH_2)_3$ . This formula brings out especially, firstly, the difference of one of the nitrogen atoms from the other three, as shown by the formation of only one hydrochloride, &c., by hexamethylenetetramine; and, secondly, its behaviour as a tertiary amine; it also serves to explain the formation of the dinitrosopentamethylenetetramine obtained by Griess and Harrow (*Abstr.*, 1888, 1268). The authors are of opinion that the study of the aliphatic amines obtained by submitting the tetramine to the action of acids is of no value in deducing its constitution, as the first products would be ammonia and formaldehyde, which have been shown by Plöchl

(Abstr., 1888, 1051) to react, forming amines. They find on reducing hexamethylenetetramine in acid solution by means of zinc dust that Plöchl's reaction does not take place, as carbonic anhydride is not evolved; further, that mono- and tri-methylamine, instead of dimethylamine, are formed.

T. H. P.

**Methylpropylketoxime and Secondary Amylamine.** By NICOLAI KURSANOFF (*Chem. Centr.*, 1898, ii, 473—474; from *J. Russ. Chem. Soc.*, 1898, 30, 269—272).—*Methylpropylketoxime* boils at 168° under 748 mm. pressure, has a sp. gr. 0.92369 at 0° and 0.90711 at 20°, and when reduced in alcoholic solution with sodium, yields *secondary amylamine*,  $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \text{Me}$ , which boils at 90° under 756 mm. pressure, and has a sp. gr. 0.75449 at 0° and 0.73839 at 20°. The hydrochloride, hydrobromide, nitrate, sulphate, platinochloride, and aurichloride of the latter compound were prepared.

E. W. W.

**Hexa-alkylated Diarsonium Compounds.** By ALFRED PARTHEIL, E. AMORT, and A. GRONOVER (*Arch. Pharm.*, 1899, 237, 127—148).—When an aliphatic iodide is heated with arsenic mercuride [prepared freshly (see this vol., ii, 417) and dried under diminished pressure] at 120°, or occasionally at 180°, the product is a yellow diarsonium mercuriodide,  $\text{As}_2\text{R}_6\text{I}_2 \cdot 2\text{HgI}_2$ ; this can be washed with ether and crystallised from alcohol. Methylic, ethylic, propylic, isopropylic, butylic, and allylic iodides react in this manner; so also benzylic iodide, but not phenylic iodide. By treatment with freshly precipitated silver chloride, the mercuriodide is converted into the compound  $\text{As}_2\text{R}_6\text{I}_2 \cdot 2\text{HgCl}_2$ . With moist silver oxide, it yields the corresponding base,  $\text{As}_2\text{R}_6(\text{OH})_2$ ; this was not isolated; it forms an alkaline solution which absorbs carbonic anhydride, and by neutralising this solution with the respective acids, the chloride, iodide, oxalate, &c., can be prepared, and from the chloride, the mercurichloride, platinochloride, and aurichloride may be obtained.

In the case of the propylic compounds, the crude base, hexapropyl-diarsonium hydroxide,  $\text{As}_2\text{Pr}_6(\text{OH})_2$ , left on evaporation of the alcoholic solution, was distilled in a current of hydrogen in an oil-bath at 240°; the distillate contained tripropylarsine oxide, which was isolated by means of its compound with mercuric chloride, together with a substance of pronounced reducing power, doubtless dipropylarsine. Presumably, the decomposition took place according to the equation,  $\text{As}_2\text{Pr}_6(\text{OH})_2 = \text{AsPr}_3\text{O} + \text{AsHPr}_2 + \text{PrOH}$ ; propylic alcohol could not be detected, however, probably owing to the small amount of it present. If the distillate is allowed to remain in the air, crystals of propylcadodylic acid,  $\text{AsPr}_2\text{O} \cdot \text{OH}$ , are obtained; these must be formed by oxidation of the dipropylarsine.

Allylic iodide reacts with arsenic mercuride when the two substances are simply boiled together in an open vessel, and in this case an attempt was made to ascertain the nature of the reaction. It appears to take place according to the equation  $\text{As}_2\text{Hg}_3 + 8\text{C}_3\text{H}_5\text{I} = \text{As}_2(\text{C}_3\text{H}_5)_6\text{I}_2 \cdot 2\text{HgI}_2 + \text{HgI}_2 + (\text{C}_3\text{H}_5)_2$  (diallyl), but at the same time a part of the allylic iodide decomposes into allylene and hydrogen iodide.

The compounds prepared are enumerated below, with their melting points and colour; as a rule, they crystallise well. Hexapropyl-diarsonium compounds: *mercuriodide*,  $\text{As}_2\text{Pr}_6\text{I}_2, 2\text{HgI}_2$ ,  $120^\circ$ , yellow; *mercuriodochloride*,  $\text{As}_2\text{Pr}_6\text{I}_2, 2\text{HgCl}_2$ ,  $150^\circ$ ; *mercurichloride*,  $\text{As}_2\text{Pr}_6\text{Cl}_2, 2\text{HgCl}_2$ ,  $169^\circ$ ; *platinochloride*,  $\text{As}_2\text{Pr}_6\text{Cl}_2, \text{PtCl}_4$ ,  $189^\circ$ , yellow;  $\text{AsPr}_3\text{O}, 2\text{HgCl}_2$ ,  $60-60.5^\circ$ ; *dipropylarsinic (propylcacodylic) acid*,  $\text{AsPr}_3\text{O}\cdot\text{OH}$ ,  $123^\circ$ . Hexamethyldiarsonium compounds: *mercuriodide*,  $\text{As}_2\text{Me}_6\text{I}_2, 2\text{HgI}_2$ ,  $184^\circ$ , yellow; *iodide*,  $171^\circ$ ; *mercurichloride*,  $\text{As}_2\text{Me}_6\text{Cl}_2, 2\text{HgCl}_2$ ,  $211^\circ$ ; *platinochloride*, unmelted at  $260^\circ$ , yellow. Hexethyl-diarsonium compounds: *mercuriodide*,  $\text{As}_2\text{Et}_6\text{I}_2, 2\text{HgI}_2$ ,  $112^\circ$ ; *iodide*,  $162^\circ$ ; *mercurichloride*,  $\text{As}_2\text{Et}_6\text{Cl}_2, 2\text{HgCl}_2$ ,  $162^\circ$ ; *platinochloride*,  $\text{As}_2\text{Et}_6\text{Cl}_2, \text{PtCl}_4$ ,  $237^\circ$ , yellow. Hexisopropyl-diarsonium compounds: *mercuriodide*,  $\text{As}_2\text{Pr}_6\text{I}_2, 2\text{HgI}_2$ ,  $114^\circ$ , yellow; *iodide*,  $150^\circ$ ; *mercurichloride*,  $\text{As}_2\text{Pr}_6\text{Cl}_2, 2\text{HgCl}_2$ ,  $171^\circ$ ; *platinochloride*,  $\text{As}_2\text{Pr}_6\text{Cl}_2, 2\text{PtCl}_4$ ,  $211^\circ$ , yellow. Hexa-(normal)butyl-diarsonium compounds: *mercuriodide*,  $\text{As}_2\text{Bu}_6\text{I}_2, 2\text{HgI}_2$ ,  $109^\circ$ , yellow; *iodide*,  $146^\circ$ ; *platinochloride*,  $\text{As}_2\text{Bu}_6\text{Cl}_2, \text{PtCl}_4$ ,  $147^\circ$ , yellow. Hexallyldiarsonium compounds: *mercuriodide*,  $\text{As}_2\text{Al}_6\text{I}_2, 2\text{HgI}_2$ ,  $62.5-63^\circ$ , yellow;  $\text{As}_2\text{Al}_6\text{I}_2, \text{HgCl}_2$ ,  $72.5^\circ$ . Hexabenzyl-diarsonium compounds: *mercuriodide*,

$\text{As}_2(\text{CH}_2\text{Ph})_6\text{I}_2, 2\text{HgI}_2$ ,  $163^\circ$ , yellowish; *chloride*,  $\text{As}_2(\text{CH}_2\text{Ph})_6\text{Cl}_2$ ,  $138-140^\circ$  when crystallised with  $1\frac{1}{2}$  mols. of chloroform,  $141-142.5^\circ$  when crystallised with  $4\text{H}_2\text{O}$ ; *mercurichloride*,  $\text{As}_2(\text{CH}_2\text{Ph})_6\text{Cl}_2, 2\text{HgCl}_2$ ,  $175.5^\circ$ ; *platinochloride*,  $\text{As}_2(\text{CH}_2\text{Ph})_6\text{Cl}_2, \text{PtCl}_4 + \text{H}_2\text{O}$ ,  $196-198^\circ$ ; *aurichloride*,  $\text{As}_2(\text{CH}_2\text{Ph})_6\text{Cl}_2, 2\text{AuCl}_3$ , yellow.

C. F. B.

**Precipitation of Acetone with Mercuric Sulphate.** By CARL OPPENHEIMER (*Ber.*, 1899, 32, 986-988).—The precipitate produced by the action of mercuric sulphate on acetone was stated by Denigès (this vol., ii, 256) to have the composition  $6\text{HgSO}_4, 9\text{HgO}, 4\text{COMe}_2$  when dried at  $100^\circ$ , and  $2\text{HgSO}_4, 3\text{HgO}, \text{COMe}_2$  when dried at  $110^\circ$ . It is here stated that the precipitate does not lose in weight to any appreciable extent when heated at  $110^\circ$ , and its composition is intermediate between those corresponding with the two formulæ of Denigès. For the estimation of acetone, the factor 0.052 gives better results than the factor 0.06 deduced from the formula assigned to the precipitate.

T. M. L.

**Nitracetone.** By LOUIS HENRY (*Ber.*, 1899, 32, 865-867. Compare Lucas, this vol., i, 433).—Nitroisopropyl alcohol has no perceptible odour; it boils at  $200-201^\circ$  under 768 mm. pressure, dissolves in water, and readily yields the acetyl derivative with acetic chloride. Nitracetone has a penetrating odour, is insoluble in water, boils at  $152^\circ$  under 767 mm. pressure, and is indifferent towards acetic chloride. It combines with sodium ethoxide, yielding the compound,  $\text{C}_3\text{H}_4\text{NO}_3\text{Na}$ , produces a crystalline derivative with piperidinomethylic alcohol, and also acts vigorously on phenylhydrazine.

M. O. F.

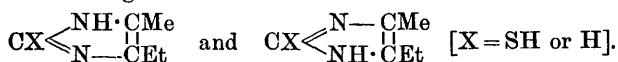
**Acetone Oils.** By A. BUISINE and P. BUISINE (*Compt. rend.*, 1899, 128, 561-562).—For the technical examination of acetone oils,

the authors determine the sp. gr., the solubility in water, the solubility in sodium hydrogen sulphite solution of 30° B., and the volume of the liquid that distils between different intervals of temperature. Acetone oil, from suint, of sp. gr. 0.830 to 0.835 at 15°, contains less than 5 per cent. of ordinary acetone, but at least 90 per cent. of ketones, 75 per cent. of which are soluble in water and consist mainly of methyl ethyl ketone.

Acetone oil of sp. gr. 0.842 from calcium pyrolignite contains a much smaller quantity of ketones boiling below 90°, and a much larger quantity of ketones boiling above 100°. C. H. B.

**Acetone Oil from Calcium Pyrolignite as a Source of Methyl Propyl Ketone.** By A. BUISINE and P. BUISINE (*Compt. rend.*, 1899, 128, 885—887. Compare Abstr., 1898, i, 175, 352).—Calcium pyrolignite contains, besides calcium acetate, small quantities of the corresponding salts of the homologues of acetic acid; in consequence of this, crude acetone, on rectification, yields about 5 per cent. of an oil distilling above 70°. From 44—68 per cent. of this "acetone oil" is insoluble in water, but only 6—8 per cent. is insoluble in sodium hydrogen sulphite; it consists largely of methyl propyl ketone and methyl isopropyl ketone, the normal isomeride predominating; traces of methyl ethyl ketone are also present. In order to separate the principal constituents, the oil is treated with excess of a concentrated solution of sodium hydrogen sulphite; the precipitate produced is decomposed with warm sodium carbonate solution and the oil which results is dried over potassium carbonate and fractionated. The constituents of the mixture are identified by means of their semicarbazides. One sample of acetone oil treated in this way yielded 45 per cent. of the two isomerides. G. T. M.

**Amidodiethyl Ketone and Amidodiethylcarbinol.** By ERNST JÄNECKE (*Ber.*, 1899, 32, 1095—1103).—*Amidodiethyl ketone*,  $\text{NH}_2\cdot\text{CHMe}\cdot\text{COEt}$ , is obtained by reducing isonitrosodiethyl ketone (Claisen and Manasse, Abstr., 1889, 585) with stannous chloride and hydrochloric acid; the deliquescent *hydrochloride*, and the yellow *picrate* and *platinochloride* melt at 128°, 132°, and 154° respectively. The base itself cannot be isolated, diethyldimethylpyrazine being obtained instead. When the hydrochloride is warmed with potassium thiocyanate, a methylethylimidazolyl- $\mu$ -mercaptan is obtained, and when this is oxidised with warm dilute nitric acid or boiled with ethylnitrite in alcoholic solution, it yields a methylethylimidazole (ethylmethyglyoxaline). These substances appear to be identical with those previously obtained from methyl amidopropyl ketone,  $\text{NH}_2\cdot\text{CHEt}\cdot\text{COMe}$  (Gabriel and Posner, Abstr., 1894, i, 355), and hence each must be capable of existing in two tautomeric forms.



With potassium cyanate in aqueous solution, the hydrochloride of

amidodiethyl ketone yields a methylethylimidazolone,  $\begin{matrix} \text{CMe} \cdot \text{NH} \\ | \\ \text{Cet} \cdot \text{NH} \end{matrix} > \text{CO}$ , identical with that obtained from methyl amidopropyl ketone (*loc. cit.*).

When methylethylglyoxime,  $\text{NOH} \cdot \text{CMe} \cdot \text{Cet} \cdot \text{NOH}$  (Claisen and Manasse, *loc. cit.*), is reduced with stannous chloride and hydrochloric acid, it does not yield the diamine,  $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CHEt} \cdot \text{NH}_2$ , but a mixture of the hydrochlorides of methyl amidopropyl and of amidodiethyl ketones.

*Amidodiethylcarbinol*,  $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CHEt} \cdot \text{OH}$ , is obtained when the hydrochloride of amidodiethyl ketone is reduced in ice cold aqueous solution by adding normal hydrochloric acid and 2½ per cent. sodium amalgam in successive small portions until the solution no longer reduces Fehling's solution. It is obtained in better yield, however, when isonitrodiethyl ketone is reduced in the same manner. It boils at 169—173°, and has a sp. gr. 0.9289 at 23.5°; the yellow *platinochloride* melts at 154°. With phenylthiocarbimide, it unites, forming *phenylhydroxyamylthiocarbamide*,  $\text{NPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{CHMe} \cdot \text{CHEt} \cdot \text{OH}$ ; this melts at 96° and when heated with strong hydrochloric acid for 6 hours at 100°, yields yellowish-brown *μ-phenylpentylene-ψ-thio-*

*carbamide*,  $\text{NPh} \cdot \text{C} \begin{matrix} \text{NH} \cdot \text{CHMe} \\ \text{S} - \text{CHEt} \end{matrix}$ ; this melts at 129°, and its yellow *picrate* at 189°. The analogous *ethyl* derivatives were prepared by using ethyl-, instead of phenyl-thiocarbimide; the thiocarbamide melts at 104—105°; the *ψ*-thiocarbamide is an oil, but its *picrate* melts at 123°. When the carbinol is heated with concentrated hydrobromic acid at 100°, it forms 3-bromo-2-amidopentane,  $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CHEt} \cdot \text{Br}$ ; the *hydrobromide* of this melts at 139°, the yellow *picrate* at 165°. With benzoic chloride and dilute caustic potash, the solution being shaken and cooled, the hydrobromide yields *μ-phenyl-β-methyl-α-ethyl-*

*oxazoline*,  $\text{CPh} \begin{matrix} \text{N} \cdot \text{CHMe} \\ \text{O} \cdot \text{CHEt} \end{matrix}$ , which boils at 160—162° under a pressure of 35—37 mm., decomposing to some extent, and forms a yellow *picrate* melting at 138°; with carbon bisulphide and caustic potash in cooled aqueous alcoholic solution, it yields *μ-mercapto-β-methyl-α-ethyl-* *thiazoline*,  $\text{SH} \cdot \text{C} \begin{matrix} \text{N} \cdot \text{CHMe} \\ \text{S} \cdot \text{CHEt} \end{matrix}$ , which melts at about 70°. C. F. B.

**The Silver Salts of *d*-, *l*-, and *dl*-Methylethylacetic Acid and the Synthesis of *d*-Valeric Acid.** By WILHELM MARCKWALD (*Ber.*, 1899, 32, 1089—1094).—Küster (Abstr., ii, 549) has made certain assumptions in the calculation which leads him to conclude that inactive silver valerate exists in solution as a racemic compound. These assumptions are not altogether justifiable, and his conclusion is invalidated thereby.

In this connection, the solubility of inactive silver valerate (methylethylacetate) has been redetermined, and found to be considerably less than has been stated hitherto. Either excess of the salt was shaken with water for six hours, or a hot, saturated solution was cooled, and then shaken for six hours with the salt that had separated out. The solution was then filtered, and titrated with N/20 ammonium thiocyanate; it was first made acid with sulphuric acid, as ferric valerate is insoluble in

neutral solution; 100 c.c. of the saturated solution contain, at 16°, 0.880, at 20°, 0.940 gram of the salt. When water is shaken with excess of both the inactive and the *l*-salt, or when a saturated solution of the *l*-salt is shaken with excess of the inactive salt, the resulting solution is found in both cases to contain the above amount of salt per 100 c.c., and to be optically inactive, whereas the undissolved solid yields an active solution. It must follow from this that the inactive silver salt is merely a conglomerate of the *d*- and *l*-forms, and not a racemic compound; otherwise, the solution would have been laevorotatory in both cases, and would have contained an amount of silver salt corresponding to the sum of the solubilities of the inactive and *l*-salts.

Advantage may be taken of these facts to obtain synthetical *d*-valeric acid in a pure state. The impure acid with  $\alpha_D = +10^\circ$  in a 100 mm. tube (Abstr., 1896, i, 203), containing about 80 per cent. of the *d*-acid, was converted into the silver salt, enough water being used to keep all the *l*-salt along with an equal amount of *d*-salt in solution. The *d*-silver salt which crystallised out was recrystallised from water and converted into the acid; this boiled constantly at 174°, and had the rotation  $\alpha_D = +8^\circ 10'$  in a 5 cm. tube at the ordinary temperature; the solubility of the silver salt is 0.680 gram per 100 c.c. at 16°, and 0.730 at 20°. This acid is identical with that obtained by Taverne (Abstr., 1895, i, 119) by hydrolysing convolvulin; the solubility of the silver salt prepared from a sample of Taverne's acid was 0.732 gram per 100 c.c. (compare also Abstr., 1896, i, 203—204, for solubilities of the *l* and inactive *dl* salt).

C. F. B.

**Rancidity of Fats.** By ALBERTO SCALA (*Bied. Centr.*, 1899, 28, 196—198; from *Staz. sper. agrar. ital.*, 1897, 613).—Olive oil, pig's fat, and butter, when rancid, showed greatly diminished iodine numbers, and contained less non-volatile fatty acids than when fresh, whilst the refractive index, the volatile fatty acids, and the ether numbers increased.

Further experiments with olive oil, pig's fat, and tallow showed that, when exposed to air and light, olive oil gained 9 per cent., pig's fat 3.5 per cent., whilst tallow (with an iodine number of only 25) gained only 1.5 per cent., oleic acid gained 8.35 per cent., whilst stearic and palmitic acids lost slightly in weight.

It is therefore concluded that rancidity depends alone on the oxidation of oleic and other acids of that series. Very rancid olive oil yielded cenanthaldehyde when distilled with steam. Hydrolysis produced formic, acetic, butyric, and ceanthic acids; also some non-volatile acids,  $C_nH_{2n-2}O_n$ , including azelaic and sebacic acids.

In rancid oleic acid, the same compounds were detected, and, in addition, a solid substance (dihydroxystearic acid) which causes opacity and viscosity. The increase of density observed in rancid fats is partly due to the production of solids.

N. H. J. M.

**Two Modifications of Ethylic  $\beta$ -Amidocrotonate.** By EMIL KNOEVENAGEL (*Ber.*, 1899, 32, 853—857. Compare Behrend, this vol., i, 331).—The two forms of ethylic  $\beta$ -amidocrotonate described by Behrend (*loc. cit.*) have been also obtained by the author, and solidify at 23—24° and 34° respectively. Both forms have a sp. gr. 1.0144



at  $36^{\circ}$ , and the refractive index is also the same in each case; the behaviour of each form towards ethylic benzylideneacetoacetate (compare Abstr., 1898, i, 447) is also identical, and on these grounds the author regards the two modifications as physical isomerides.

M. O. F.

**Isomeride of Hydroxymenthyllic Acid.** By GEORGES LÉSER (*Compt. rend.*, 1899, 128, 734—736).—When acetylmethylheptenone is mixed at the ordinary temperature with six times its weight of 80 per cent. sulphuric acid, it is mainly converted into a mixture of two compounds,  $C_{10}H_{16}O_2$  and  $C_{10}H_{14}O$ , which boil at  $125$ — $135^{\circ}$  under 20 mm. pressure and are soluble in ether. The mixture gives the  $\beta$ -diketone reaction with ferric chloride, and when treated with potassium methoxide in excess of methylic alcohol, yields an oily liquid volatile in steam and the potassium salt of an acid,  $C_{10}H_{18}O_3$ . This acid boils at  $190$ — $191^{\circ}$  under 20 mm. pressure, and melts at  $98^{\circ}$ ; it forms a deliquescent barium salt and a crystallisable silver salt soluble in water and stable when exposed to light. The ethylic salt boils at  $149^{\circ}$  under 20 mm. pressure and has a strong, fruity odour; the oxime crystallises from dilute alcohol in small, brilliant prisms which melt at  $98^{\circ}$ . The acid is isomeric with Arth's hydroxymenthyllic acid and with Baeyer's isopropylheptanonic acid; most probably it is isopropyl-4-heptanone-6-oic acid.

C. H. B.

**Solubility of the Normal Acids of the Oxalic Series.** By F. LAMOUROUX (*Compt. rend.*, 1899, 128, 998—1000).—Henry (Abstr., 1885, 335) stated that the dibasic acids of the oxalic series containing an even number of carbon atoms are slightly soluble in water, whilst those containing an odd number of carbon atoms are readily soluble. In the case of the second group, the solubility of the three initial members only had been determined. The author finds that the third member, pimelic acid, is in reality very slightly soluble, and that the succeeding members, azelaic and brassylic acids, are as insoluble as their homologues containing an even number of carbon atoms. A table is given showing the solubility of these dibasic acids through a range of temperature from  $0^{\circ}$  to  $66^{\circ}$ , and it is shown that, in general, these acids are very insoluble in water, but that to this rule there are two exceptions, as malonic and glutaric acids readily dissolve in this solvent.

G. T. M.

**Solubility of Substituted Malonic Acids.** By GUSTAVE MASSOL and F. LAMOUROUX (*Compt. rend.*, 1899, 128, 1000—1002. Compare preceding abstract).—Determinations of the solubilities of a series of monosubstituted malonic acids show that they are all very soluble in water, and that the introduction of an alkyl radicle diminishes the solubility of malonic acid; in the case of succinic acid, the introduction of alkyl groups increases the solubility. Those substituted malonic acids containing an odd number of carbon atoms are more soluble than those containing an even number, but the difference becomes very small when the temperature is raised. When compared with the normal dibasic acids containing the same number of carbon atoms, the derivatives of malonic acid are found to be

far more soluble. These results indicate that it is not possible at present to deduce any conclusions as to the relationship between the solubility of the dibasic acids and their molecular structure.

G. T. M.

**Separation of the Dibasic Acids formed by the Oxidation of Fats.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1898, [iii], 19, 562—565).—The statement of Aerppe (*Bull. Soc. Chim.*, 1866, [ii], 5, 59), that pimelic acid is not formed by the oxidation of fats, has hitherto been generally accepted, but it is now shown that all the normal dibasic acids of the oxalic series, from succinic acid to sebacic acid, are thus produced. The process recommended for their separation comprises the following operations:—1. Heating under the ordinary pressure, until a temperature of  $230^{\circ}$  is reached, whereby the whole of the succinic acid is converted into succinic anhydride, a portion of which distils over. 2. Distillation under diminished pressure to complete the separation of succinic anhydride. 3. Treatment of the residue with ether, which leaves undissolved a mixture of pimelic and adipic acids. 4. Crystallisation of this mixture from water, whereby pure adipic acid is obtained, whilst pimelic acid remains in solution. 5. Conversion of the acids contained in the ethereal extract and the aqueous mother liquors into their calcium salts. Calcium glutarate, being very soluble in water, is easily separated from calcium pimelate, which is slightly soluble in cold, but insoluble in boiling, water.

N. L.

***aa*-Dimethylglutaric Acid.** By EDMOND E. BLAISE (*Compt. rend.*, 1899, 128, 676—678. Compare Abstr., 1898, i, 561, 631).—Cyanodimethylsuccinic acid, obtained by hydrolysing its ethereal salt (compare Abstr., 1894, i, 492), loses carbonic anhydride when heated at  $123^{\circ}$ ; this decomposition does not give rise to cyanodimethylpropionic acid, but to its isomeride, dimethylsuccinimide. The *ethylic* salt of cyanodimethylpropionic acid,  $\text{CN} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{COOEt}$ , produced by heating the monethylic salt of cyanodimethylsuccinic acid, boils without decomposition at  $217\text{--}220^{\circ}$  under atmospheric pressure. The *hydrochloride* of ethylic  $\gamma$ -amido-*aa*-dimethylbutyrate,  $\text{COOEt} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot \text{HCl}$ , obtained by reducing the preceding compound with sodium and absolute alcohol and subsequently treating the product with hydrochloric acid, crystallises in needles melting at  $112^{\circ}$ . The corresponding *hydrobromide* and *sulphate* melt at  $142^{\circ}$  and  $145^{\circ}$  respectively.

These derivatives may also be obtained by starting from *aa*-dimethylglutaric acid. The anhydride of this acid, when mixed with alcoholic ammonia, yields ammonium *aa*-dimethylglutaramate; the corresponding sodium salt, when treated in succession with alkaline hypobromite and alcoholic hydrogen bromide, gives rise to the hydrobromide melting at  $142^{\circ}$ ; from this salt, the hydrochloride and sulphate may be obtained. On attempting to liberate  $\gamma$ -amido-*aa*-dimethylbutyric acid from any one of these salts, 3:3-dimethylpyrrolidone is produced; this substance crystallises in nacreous leaflets, melts at  $65\text{--}67^{\circ}$ , and boils without decomposition at  $237^{\circ}$  under atmospheric pressure.

G. T. M.

**Formation of Olefindicarboxylic Acids from Ethylic Dibromomonalkylacetoacetates.** By MAX CONRAD (*Ber.*, 1899, **32**, 1005—1008).—The author explains the formation of mesaconic acid from ethylic  $\gamma$ -dibromo- $\alpha$ -methylacetoacetate thus:  $\text{CHBr}_2 \cdot \text{C}(\text{OH})_2 \cdot \text{CMe} \cdot \text{COOEt} \rightarrow \text{CH}(\text{OH})_2 \cdot \text{C}(\text{OH})_2 \cdot \text{CMe} \cdot \text{COOH} \rightarrow \text{C}(\text{OH})_2 \cdot \text{C} \cdot \text{CMe} \cdot \text{COOH} \rightarrow \text{COOH} \cdot \text{CH} \cdot \text{CMe} \cdot \text{COOH}$  (compare Wolff, *Abstr.*, 1891, 417, and Cloez, *Abstr.*, 1890, 739). An analogous change occurs in the case of the  $\alpha\alpha$ -dihalogen  $\beta$ -ketones (Faworsky, *Abstr.*, 1894, i, 391), which are converted into unsaturated monobasic acids. It is now shown that unsaturated tribasic acids can be produced in a similar way, for instance, ethylic dibromoacetylsuccinate has been converted into aconitic acid,  $\text{CHBr}_2 \cdot \text{CO} \cdot \text{CH}(\text{COOEt}) \cdot \text{CH}_2 \cdot \text{COOEt} \rightarrow \text{COOH} \cdot \text{CH} \cdot \text{C}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$ , by the action of baryta water.

T. M. L.

**Action of Ethylic Sodiomalonate on the Dibromides,  $\text{C}_n\text{H}_{2n}\text{Br}_2$ .** By WLADIMIR IPATIEFF (*Chem. Centr.*, 1898, ii, 660—661; from *J. Russ. Chem. Soc.*, 1898, **30**, 391—400).—*Ethylic dimethylallylmalonate*,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}(\text{COOEt})_2$ , formed by slowly adding sodium dissolved in absolute alcohol to a mixture of dibromo- $\beta$ -dimethyltrimethylene and ethylic malonate, is an oil with a pleasant odour, boils at 140—141° under 20 mm. pressure, and decolorises potassium permanganate. The *oxime* crystallises from benzene in colourless prisms and melts at 85—87°. The *acid* melts at 82·5—83·5°, is soluble in water, alcohol, and ether, quickly decolorises potassium permanganate, and when heated above the melting point loses carbonic anhydride and forms a monobasic, unsaturated acid. The calcium, sodium, and ammonium salts are easily soluble in water, but the salts of the heavy metals are insoluble. The silver salt, obtained by precipitating a solution of the ammonium salt with silver nitrate, is a white, crystalline precipitate.

By the action of ethylic sodiomalonate on dibromotrimethylethylene, trimethylethylene and ethylic ethanetetra-carboxylate are formed. Dibromisobutylene acts on ethylic sodiomalonate in a similar manner; hence, generally, all dibromides containing one bromine atom united to a tertiary and the other to a primary or secondary carbon atom react with ethylic sodiomalonate forming olefines and ethylic ethanetetra-carboxylate.

E. W. W.

**Preparation and Properties of  $\beta$ -Hydroxy- $\alpha\alpha$ -dimethylglutaric Acid.** By SERGIUS N. REFORMATSKY (*Chem. Centr.*, 1898, ii, 885—886; from *J. Russ. Chem. Soc.*, **30**, 453—466).—By the action of zinc on a mixture of ethylic bromopropionate and ethylic formate, a compound,  $\text{ZnBr} \cdot \text{O} \cdot \text{CH}(\text{CHMe} \cdot \text{COOEt})_2$ , is formed, which, when treated with water, yields ethylic  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylglutarate. By using a copper-zinc couple, a yield of 88·6 per cent. of the ethylic salt may be obtained. The corresponding *acid* crystallises best from ethylic acetate, melts at 136—137°, is easily soluble in water, ether, alcohol, glacial acetic acid, acetone, and ethylic formate, slightly in carbon bisulphide, benzene, and light petroleum, and has the electrical dissociation constant,  $k = 0\cdot0122$  (Michailenko). The *barium*, *sodium*, *potassium*, and *silver* salts were prepared.

*β*-Acetoxy- $\alpha\alpha_1$ -dimethylglutaric anhydride,  $\text{OAc}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CHMe}\cdot\text{CO} \\ \text{CHMe}\cdot\text{CO}\end{smallmatrix}\right\rangle\text{O}$ ,

prepared by the action of acetic chloride on the acid, separates in large crystals, is easily soluble in benzene, and with cold water forms the corresponding acid,  $\text{OAc}\cdot\text{CH}(\text{CHMe}\cdot\text{COOH})_2$ , which melts at  $120\text{--}121^\circ$ , is soluble in ether and chloroform, insoluble in light petroleum, has the electrical dissociation constant  $k=0\cdot0200$ , and forms a barium salt,  $\text{C}_9\text{H}_{12}\text{O}_6\text{Ba} + 3\text{H}_2\text{O}$ . The *monotoluidide* separates in a lustrous, silky mass, melts at  $129\text{--}130^\circ$ , and decomposes at  $170^\circ$  with liberation of gas. The acetyl group of the anhydride is only partially hydrolysed by alcoholic potassium hydroxide.

By the action of hydriodic acid on hydroxydimethylglutaric acid, in addition to the mixture of fumaroid and maleoid  $\alpha\alpha_1$ -dimethylglutaric acids which Auwers obtained,  $\alpha\alpha_1$ -dimethylglutaconic acid,  $\text{COOH}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CMe}\cdot\text{COOH}$ , was also formed in one experiment. This acid, which is better prepared by the action of an 80 per cent. solution of hydriodic acid on the ethylic salt or by oxidising the acid with sulphuric acid, crystallises in lustrous needles, melts at  $147^\circ$ , and is easily soluble in hot water, but only slightly so in cold.

Ethylic  $\beta$ -hydroxy- $\alpha\alpha_1$ -dimethylglutarate, when hydrolysed, yields, not only the crystalline acid, but also an acid with similar properties which separates as a syrup and is probably an isomeride; the latter acid, when heated with hydriodic acid, forms the dimethylglutaconic acid with the lower melting point, whilst by the action of sulphuric acid it yields the acid which melts at  $147^\circ$ . By the action of acetic chloride, it forms a compound which crystallises in slender needles, melts at  $132\cdot5^\circ$  and is probably the acetoxyanhydride, since with water it gives the corresponding acid which separates in large crystals, melts at  $82\cdot5\text{--}83\cdot5^\circ$  and yields a barium salt,  $\text{C}_9\text{H}_{12}\text{O}_6\text{Ba} + 2\text{H}_2\text{O}$ . The paratoluidide,  $\text{C}_{16}\text{H}_{21}\text{NO}_5$ , prepared from the anhydride melts at  $181\cdot5\text{--}182^\circ$ .

E. W. W.

**Action of Zinc on a Mixture of Ethylic Bromisobutyrate and Ethylic Formate. Synthesis of Symmetrical  $\beta$ -Hydroxytetramethylglutaric Acid.** By JACKOV. I. MICHAILENKO (*Chem. Centr.*, 1898, ii, 885; from *J. Russ. Chem. Soc.*, 30, 466—475).—Ethylic  $\beta$ -hydroxytetramethylglutarate, prepared by the action of zinc on a mixture of ethylic bromisobutyrate and ethylic formate, decomposes on distillation; hence, the portion boiling below  $200^\circ$  was distilled off and the residue hydrolysed. The acid,  $\text{OH}\cdot\text{CH}(\text{CMe}_2\cdot\text{COOH})_2$ , crystallises in short prisms, melts and decomposes at  $162\text{--}163^\circ$ , is soluble in water, alcohol, ether, and ethylic acetate, and has the electrical dissociation constant  $k=0\cdot0133$ . The *potassium*, *sodium*, *barium*, *calcium*, *lead*, and *silver* salts were prepared.

*β*-Acetoxytetramethylglutaric anhydride,  $\text{OAc}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CMe}_2\cdot\text{CO} \\ \text{CMe}_2\cdot\text{CO}\end{smallmatrix}\right\rangle\text{O}$ ,

obtained by the action of acetic chloride on hydroxytetramethylglutaric acid, melts at  $88\text{--}89^\circ$ , and when treated with water, yields the acid which crystallises in four-sided leaflets, melts at  $158\text{--}159^\circ$  and has the electrical dissociation constant  $k=0\cdot005166$ . The *potassium*, *barium*, and *silver* salts are described. The *paratoluidide*, prepared by the

action of paratoluidine on the anhydride, separates in slender, hair-like crystals and melts at 157—159°. E. W. W.

**Racemic Transformation of Potassium Racemate.** By JACOBUS H. VAN'T HOFF and WOLF MÜLLER (*Ber.*, 1899, 32, 857—859. Compare Roozeboom, this vol., ii, 276).—Potassium racemate crystallises with  $1\text{H}_2\text{O}$  (rhombic) and with  $2\text{H}_2\text{O}$  (monoclinic); both forms lose water when heated, the monohydrate undergoing this change at 30°. The dihydrate undergoes transformation into the active components at 71·78°, in accordance with the equation  $2\text{C}_4\text{H}_4\text{O}_6\text{K}_2 \cdot 2\text{H}_2\text{O} = (\rightarrow\text{C}_4\text{H}_4\text{O}_6\text{K}_2 \cdot \frac{1}{2}\text{H}_2\text{O} + \leftarrow\text{C}_4\text{H}_4\text{O}_6\text{K}_2 \cdot \frac{1}{2}\text{H}_2\text{O} + 3\text{H}_2\text{O}$ .

This behaviour resembles that of hydrogen ammonium malate (Kenrick, *Abstr.*, 1897, i, 506). M. O. F.

**Parapyruvic Acid.** By LUDWIG WOLFF (*Annalen*, 1899, 305, 154—165).—Finck observed that pyruvic acid, when treated with excess of baryta, yields a sparingly soluble basic salt which gives rise to uvitic acid under the influence of the boiling agent; carbonic anhydride converts the salt into a readily soluble normal derivative. Aqueous solutions of the pyruvates undergo slow spontaneous transformation into the salts of so-called syrupy pyruvic acid, the action being hastened by small quantities of such condensing agents as potassium cyanide, caustic potash, baryta, and ammonia; the salts obtained in this way are normal derivatives of the dibasic acid,  $\text{C}_6\text{H}_8\text{O}_6$ , but larger proportions of the condensing agent give rise to compounds allied to the basic salt obtained by Finck. The acid from which these salts are derived is termed *parapyruvic acid*; it probably has the constitution expressed by the formula,  $\text{COOH} \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{COOH}$ , and is unstable in the free condition, becoming in part converted into ketovalerolactonecarboxylic acid. Parapyruvic acid is regarded as the intermediate product in the synthesis of methylidihydrotrimesic acid from pyruvic acid, and this suggestion accounts for the difference in behaviour exhibited by acetone and pyruvic acid on condensation; it should be mentioned, however, that alkalis regenerate a small proportion of pyruvic acid from the para-acid.

Normal *barium* parapyruvate is a white, granular substance containing  $5\frac{1}{2}\text{H}_2\text{O}$ ; it is somewhat sparingly soluble in water and dilute acetic acid, but dissolves more readily in sodium acetate, and freely in hydrochloric acid, which converts it into the lactonic acid. Protracted treatment with dilute acetic acid gives rise to a modification which contains  $4\frac{1}{2}\text{H}_2\text{O}$ , and is probably identical with a salt obtained by Mulder from the basic barium salt and acetic acid. The *calcium* salt contains  $4\text{H}_2\text{O}$ . The *lead* salt is precipitated on mixing aqueous solutions of pyruvic acid and lead acetate, and crystallises in small plates.

When barium parapyruvate is decomposed with sulphuric acid, a mixture of 20 per cent. of parapyruvic acid with 80 per cent. of the lactonic acid is obtained; it forms a colourless, viscous syrup, which yields a clear solution in water, and gives no precipitate with phenylhydrazine hydrochloride. Hot concentrated sodium hydroxide converts the syrup into methylidihydrotrimesic and oxalic acids; cold alkalis

regenerate the salts of parapyruvic acid, whilst alkali carbonates yield salts of the lactonic acid. M. O. F.

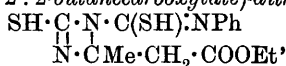
**Composition and Crystalline Form of Malates.** By HERMANN TRAUBE (*Zeit. Kryst. Min.*, 1899, 31, 160—178).—Crystallographic descriptions are given of the following salts of malic acid. The observations all agree with Pasteur's law of the enantiomorphism of crystals of optically active substances. The best method of preparing the salts is by the interaction of strontium hydrogen malate with the sulphate of the metal.

KC <sub>4</sub> H <sub>5</sub> O <sub>5</sub> + 3½H <sub>2</sub> O,	Rhombic, hemihedral,	0·5355 : 1 : 0·5471
RbC <sub>4</sub> H <sub>5</sub> O <sub>5</sub> + 3½H <sub>2</sub> O,	,,	0·4986 : 1 : 0·5136
NH <sub>4</sub> ·C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ,	,,	0·723 : 1 : 0·7726
NaC <sub>4</sub> H <sub>5</sub> O <sub>5</sub> + 2H <sub>2</sub> O,	,,	? : 1 : 0·9705
LiC <sub>4</sub> H <sub>5</sub> O <sub>5</sub> + H <sub>2</sub> O,	Tetragonal, trapezohedral,	1 : 1·2447
LiC <sub>4</sub> H <sub>5</sub> O <sub>5</sub> + 6H <sub>2</sub> O,	Monoclinic, hemimorphic,	0·3917 : 1 : 0·4890; β = 41° 12'.
Li <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + H <sub>2</sub> O,	Rhombic,	0·6556 : 1 : 0·7033
Ca(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 6H <sub>2</sub> O,	Rhombic, hemihedral,	0·9418 : 1 : 1·0556
Sr(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 6H <sub>2</sub> O,	,,	0·9646 : 1 : 0·9037
CaC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 3H <sub>2</sub> O,	,,	0·4375 : 1 : 1·0932
Mg(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 2H <sub>2</sub> O,	Tetragonal, trapezohedral,	1 : 2·0536
Zn(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 2H <sub>2</sub> O,	,,	1 : 2·0041
Cu(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 2H <sub>2</sub> O,	,,	1 : 1·9953
Mn(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 2H <sub>2</sub> O,	,,	1 : 2·0156
Co(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 2H <sub>2</sub> O,	,,	1 : 2·0245
Ni(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + 2H <sub>2</sub> O,	,,	1 : 1·9963
Cu(C <sub>4</sub> H <sub>5</sub> O <sub>5</sub> ) <sub>2</sub> + H <sub>2</sub> O,	Monoclinic, hemimorphic,	0·7663 : 1 : 0·9699; β = 86° 4'.
MgC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 3H <sub>2</sub> O,	,,	0·8579 : 1 : 0·6015; β = 74° 24'.
ZnC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 3H <sub>2</sub> O,	,,	0·8619 : 1 : 0·5762; β = 73° 42'.
MnC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 3H <sub>2</sub> O,	,,	0·8871 : 1 : 0·6692; β = 78° 30'.
CoC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 3H <sub>2</sub> O,	,,	0·9197 : 1 : 0·6386; β = 73° 0'.
MgC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 5H <sub>2</sub> O,	Rhombic, hemihedral,	0·7378 : 1 : 0·4040
MnC <sub>4</sub> H <sub>4</sub> O <sub>5</sub> + 4H <sub>2</sub> O,	,,	0·9844 : 1 : 1·1076

L. J. S.

**New Method of Preparing Ethylic Dicarbitetetracarboxylate [Ethylenetetracarboxylate].** By RUBIN BLANK and E. SAMSON (*Ber.*, 1899, 32, 860. Compare Conrad and Brückner, *Abstr.*, 1892, 39; also Bischoff, *Abstr.*, 1896, i, 130).—When anhydrous potassium carbonate acts on a solution of ethylic bromomalonate in some indifferent solvent, hydrogen bromide is eliminated and ethylic ethylenetetracarboxylate, C(COOEt)<sub>2</sub>·C(COOEt)<sub>2</sub>, produced. Ethylic chloromalonate behaves in the same way, but the action is less energetic. M. O. F.

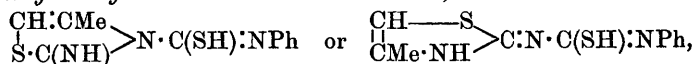
**Dithiobiurets.** By EMIL FROMM and E. PHILIPPE (*Ber.*, 1899, 32, 835—848).—*Ethylic α-phenyldithio-C-methylketuretcaboxylate* or *α-phenyl b : c- (ethylic 2 : 2-butanecarboxylate)-dithiobiurimine*,



formed when hydrogen chloride is passed into a mixture of phenylthiobiuret and ethylic acetoacetate, separates from alcohol in colourless crystals, melts at 219—220°, and dissolves somewhat readily in glacial acetic acid, but only sparingly in water and alcohol; the corresponding *acid*, C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>S<sub>2</sub>O<sub>2</sub>, made by hydrolysing the ethereal salt with dilute alcoholic soda, crystallises in slender, white needles,

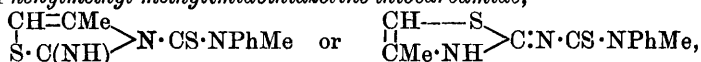
and melts at 214—216°; when shaken with benzylic chloride and dilute soda, it yields a *dibenzyl-benzylic* salt,  $C_{33}H_{31}N_3S_2O_2$ , which crystallises from alcohol in colourless needles and melts at 133°. When the acid is heated with acetic anhydride, it gives a mixed anhydride,  $\begin{array}{c} \text{CS-N} \cdot \text{CS-NHPh} \\ | \quad | \\ \text{NH} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{COOAc} \end{array}$ , which becomes crystalline when the cooled product is left during 24 hours, but cannot be crystallised from acetic acid, as it decomposes very readily in presence of moisture; it may be purified by dissolution in cold acetone and precipitation with light petroleum, when it separates in colourless crystals melting at 168°.

*Phenyl-methylimidothiazoline-thiocarbamide,*



is obtained as the *hydrochloride*,  $C_{11}H_{11}N_3S_2 \cdot \text{HCl}$ , by warming phenyldithiobiuret with twice its weight of monochloroacetone; this separates as a crystalline mass, and may be purified by crystallisation from alcohol, when it forms shining, white needles, melts at 163°, and is insoluble in ether, but dissolves sparingly in water and readily in alcohol; the *base* separates on spontaneous evaporation of its ethereal solution in light yellow crystals, and melts and decomposes at 163°. The *benzyl* derivative,  $C_{18}H_{17}N_3S_2$ , forms colourless crystals and melts at 89—90°.

*Phenylmethyl-methylimidothiazoline-thiocarbamide,*



is obtained as the *hydrochloride*,  $C_{12}H_{13}N_3S_2 \cdot \text{HCl}$ , melting at 216°, when phenylmethylthiobiuret is warmed with monochloroacetone on a water-bath. The *base*, obtained by dissolving the salt in alcohol and precipitating with water, separates from ether in radiating crystals, melts at 84°, and is insoluble in water, but dissolves readily in alcohol and ether; it does not give a benzyl derivative on treatment with soda and benzylic chloride.

When phenyldithiobiuret is warmed with four times its weight of acetic anhydride, it dissolves, turns brown, and finally hydrogen sulphide is evolved; if, before the last stage, the liquid is poured into water, a mixture of crystalline substances is obtained, and on dissolving this in boiling alcohol and allowing to cool, *monacetyldithiobiuret*,  $C_{10}H_{11}N_3S_2O$ , separates, whilst the mother liquor yields the *diacetyl* compound,  $C_{12}H_{13}N_3S_2O_2$ ; both crystallise in yellow needles, the former melting at 184° and the latter at 193°. A. L.

**Mercury Substitution Derivatives of Alcohol and Acetic Acid.** By KARL A. HOFMANN (*Ber.*, 1899, 32, 870—880. Compare this vol., i, 97).—The compound,  $C_2H_4HgCl_4$ , obtained by the action of mercuric chloride on absolute alcohol under the influence of sodium ethoxide or sodium acetate, forms a white powder resembling calomel; it immediately becomes black when treated with ammonia, potassium cyanide, or caustic alkalis, and yields mercury with a hot mixture of caustic soda and potassium cyanide, the odour of aldehyde resin

becoming perceptible. Hot alkalis convert the substance into a black residue and a colourless solution, from which hydrochloric acid precipitates trimercuracetic acid. A boiling solution of hydrazine hydrate eliminates all the mercury, and forms a compound of hydrazine and aldehyde, with liberation of 4.3 per cent. of nitrogen; in consequence of this result, the author ascribes to the mercury derivative a constitution expressed by the formula

$\text{Hg} \begin{array}{c} \text{CCl} \cdot \text{HgCl} \\ | \\ \text{C}(\text{HgCl})_2 \end{array}$ . When the substance is heated with mercuric oxide and caustic alkali at 105—110°, dimercuracetic and trimercuracetic acids are produced, along with the explosive base,  $\text{C}_2\text{Hg}_6\text{O}_4\text{H}_2$  (Abstr., 1898, i, 635).

The compound,  $\text{C}_2\text{Hg}_3\text{Cl}_4$ , obtained by passing acetylene into a solution of mercuric and sodium chlorides, yields aldehyde when treated with boiling dilute hydrochloric acid, and probably has the constitution

$\text{Hg} \begin{array}{c} \text{CCl}_2 \\ | \\ \text{C}(\text{HgCl})_2 \end{array}$ .

When sodium acetate, mercuric oxide, and potassium hydroxide are heated with water on a sand-bath until the oxide disappears, a yellowish-white substance is formed. When this is repeatedly digested with 5 per cent. aqueous potash, a compound,  $(\text{C}_2\text{Hg}_2\text{O}_3\text{H}_2)_x$ , is left undissolved, whilst the *hydroxydimercuracetic acid*,  $\text{OH} \cdot \text{CHg}_2 \cdot \text{COOH}$ , goes into solution and forms a yellow, gelatinous precipitate when dilute nitric acid is added. The residue yields the compound  $\text{C}_2\text{Hg}_2\text{NO}_5\text{H}$  when treated with 3 per cent. nitric acid. Dilute hydrochloric acid converts hydroxydimercuracetic acid into the *chloride*,  $\text{C}_2\text{Hg}_2\text{Cl}_2\text{O}_2\text{H}_2$ , and dilute nitric acid gives rise to the *nitrate*,  $\text{C}_2\text{Hg}_2\text{NO}_5\text{H}$ , which forms a yellowish-white powder.

The compound  $\text{C}_2\text{Hg}_3\text{IO}_3\text{H}$ , obtained by heating sodium acetate with mercuric iodide and caustic alkali, forms lustrous, greenish-white leaflets; the *sodium* salt is the direct product, and crystallises in yellow leaflets. The compound  $\text{C}_2\text{Hg}_3\text{NO}_7\text{H}_3$  is prepared by the action of a dilute solution of silver nitrate.

The compound  $\text{HgCl} \cdot \text{CHCl} \cdot \text{COOK}$ ,  $\text{KCl}$ , produced on heating aqueous potassium monochloracetate with mercuric oxide, crystallises from alcohol in slender, white needles.

M. O. F.

**Mercury Derivatives of Nitrogen Compounds.** By KARL A. HOFMANN and EDUARD C. MARBURG (*Annalen*, 1899, 305, 191—222).—The authors give evidence in favour of the formula  $\text{NH}_2 \cdot \text{HgCl}$  for the infusible white precipitate obtained when a solution of mercuric chloride is treated with ammonia. A boiling 20 per cent. solution of potassium hydroxide eliminates all the nitrogen from this substance in the form of ammonia; Kane's statement to the effect that only one-half is eliminated led Rammelsberg to suggest the formula  $\text{NHg}_2\text{Cl} \cdot \text{NH}_4\text{Cl}$ .

The fusible white precipitate obtained when ammonia is added to a solution of mercuric chloride containing a large proportion of ammonium chloride has the constitution expressed by the formula  $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ ; the formula  $\text{NHg}_2\text{Cl} \cdot 3\text{NH}_4\text{Cl}$  has been put forward by Rammelsberg and Pesci, but the authors have found no reason for believing one atom of nitrogen to be in a condition of combination different from



that of the other. When the gases from nitric acid and arsenious oxide are passed into a suspension of the fusible, white precipitate in absolute alcohol, the salt is resolved into mercuric chloride and ammonia, yielding the double compound,  $\text{HgCl}_2 \cdot 2\text{NH}_4\text{NO}_3$ , which crystallises from methylic alcohol in long, lustrous needles; hot sulphuric acid liberates chlorine. The double compound,  $\text{HgCl}_2 \cdot 2\text{C}_6\text{H}_4\text{N}_2\text{SO}_3$ , obtained when a suspension of the fusible white precipitate and diazobenzene-sulphonic acid is allowed to remain at  $10-15^\circ$  during several days, forms straw-yellow crystals which decompose and dissolve in water, the whole of the nitrogen being liberated when the liquid is boiled; potassium hydroxide develops a yellow coloration, and sodium carbonate a reddish tint, whilst ammonia precipitates mercury and liberates nitrogen. The double compound,  $\text{Hg}(\text{CN})_2 \cdot 2\text{C}_6\text{H}_4\text{N}_2\text{SO}_3$ , prepared from mercuric cyanide and diazobenzene-sulphonic acid, forms lustrous, prismatic crystals, and loses nitrogen when treated with boiling acids or alkalis; water at  $60^\circ$  resolves it into mercuric cyanide and diazobenzene-sulphonic acid.

Ethylamine forms three compounds with mercuric chloride, of which those having the formulæ  $\text{NH}_4\text{Et} \cdot \text{HgCl}$  and  $\text{NH}_4\text{Et} \cdot \text{HgCl}_2$  have been prepared by Köhler. The double compound,  $\text{Hg}(\text{NH}_2\text{Et})_2\text{Cl}_2$ , obtained on adding liquid ethylamine to alcoholic mercuric chloride, crystallises from alcohol in white leaflets and melts and decomposes at  $185^\circ$ . The double compound,  $\text{NHMe}_2 \cdot \text{HgCl}_2$ , prepared from alcoholic solutions of dimethylamine and mercuric chloride, crystallises from boiling alcohol in nacreous leaflets, and melts at  $172^\circ$ ; aqueous solutions yield an orange yellow powder, having the composition  $\text{Hg}_3\text{Cl}_2\text{O}_2 \cdot \text{NHMe}_2 \cdot \text{HCl}$ . The double compound,  $2\text{NMe}_3 \cdot 3\text{HgCl}_2$ , derived from mercuric chloride and trimethylamine, separates from alcohol in white crystals.

Millon's base is prepared from yellow mercuric oxide and aqueous ammonia, and may be regarded as dihydroxymercuriammonium hydroxide,  $\text{NH}_2(\text{Hg} \cdot \text{OH})_2 \cdot \text{OH}$ ; there is no justification for representing it by the formula  $\text{NHg}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$ , put forward by Rammelsberg. When the freshly prepared base is protected from light and dried over caustic potash in an atmosphere of ammonia, it becomes darker and more sensitive to light, and then has the composition  $\text{NHg}_2\text{O}_3\text{H}_3$ ; if it is dried in a vacuum over sulphuric acid, ammonia is eliminated and a dark brown powder of the composition  $\text{NHg}_3\text{O}_2\text{H}$  is produced. Absolute alcohol dehydrates Millon's base, mercuric oxide being the final product; alcoholic ammonia, therefore, cannot be used in preparing the substance. The compound,  $\text{NHg}_2 \cdot \text{OH}$ , obtained by heating Millon's base at  $125^\circ$  in an atmosphere of ammonia, is a dark brown powder which explodes sharply on detonation, or when heated at  $130^\circ$ ; when exposed to air, it absorbs moisture, acquiring a lighter colour and losing its explosive properties. This explosive substance is also obtained when dried, yellow mercuric oxide is heated at  $120^\circ$  in an atmosphere of ammonia; it has been prepared also by Weyl. The nitrate, bromide, and chloride of Millon's base are described in the paper.

When the explosive compound,  $\text{N}_2\text{H}_2\text{Hg}_2\text{Cl}_2$ , obtained from hydrazine sulphate and mercuric chloride (Hofmann and Marburg, *Abstr.*, 1897, ii, 554), is treated with acetic anhydride, it yields the compound

$\text{NHg} \cdot \text{NAC}_2$ . *Diacetylhydrazine*,  $\text{N}_2\text{H}_2\text{Ac}_2$ , obtained by the action of hydrogen sulphide on this substance, crystallises from alcohol in lustrous leaflets and melts at  $132^\circ$ ; the *benzylidene* derivative crystallises from ether and melts at  $113^\circ$ . On treating the compound  $\text{N}_2\text{H}_2\text{Hg}_2\text{Cl}_2$  with chlorine in presence of carbon tetrachloride, it yields the compound  $\text{HgCl}_2 \cdot \text{N}_2\text{H}_4 \cdot \text{HCl}$  in lustrous leaflets melting at  $157^\circ$ .

The double compound,  $\text{N}_2\text{H}_4 \cdot \text{Cu}(\text{NO}_3)_2$ , is bluish-green, and explodes when heated and on detonation. M. O. F.

**Aliphatic Sulphonic Acids. III.** By ELMER P. KOHLER (*Amer. Chem. J.*, 1899, 21, 349—370. Compare Abstr., 1898, i, 168, and this vol., i, 19).— $\alpha$ -Bromethylenesulphonic acid,  $\text{CH}_2\text{:CBr} \cdot \text{SO}_3\text{H}$ , is fairly stable in dilute aqueous solution, but when the solution is evaporated in a vacuum or over phosphoric anhydride a point is reached beyond which it is impossible to concentrate the acid without decomposition ensuing, hydrogen bromide and sulphurous anhydride being evolved. The *potassium*, *sodium*, and *barium* salts have all been obtained in the anhydrous form. *Bromethylenesulphonic chloride*,  $\text{CH}_2\text{:CBr} \cdot \text{SO}_2\text{Cl}$ , obtained by the action of phosphorus pentachloride on the potassium salt suspended in chloroform, is an oily liquid which cannot be distilled and which does not solidify at  $-20^\circ$ . Oxidising agents convert the acid into carbonic anhydride, sulphuric acid, hydrogen bromide, and water. Reducing agents, both neutral and acid, convert the brom-acid quantitatively into ethylenesulphonic acid, and when an alkaline solution of the potassium salt is boiled with a large excess of mercuric chloride, the bromine is slowly replaced by chlorine.

Bromethylenesulphonic acid combines with water more readily even than does ethylenesulphonic acid, slow combination taking place when aqueous solutions of the acid or of its salts are boiled, whilst at  $120^\circ$  combination is complete in less than three hours. In the presence of a small quantity of an alkali carbonate, or an inorganic acid, addition takes place very readily at, or even below,  $100^\circ$ , the product formed in all cases being  $\alpha$ -bromo- $\beta$ -hydroxyethanesulphonic acid. So far the acid has not been obtained in a crystalline form; the *sodium* salt crystallises from water in characteristic conical aggregates and the *potassium* salt in small, lustrous prisms containing  $\frac{1}{2}\text{H}_2\text{O}$ , which it loses below  $150^\circ$ ; when the anhydrous potassium salt is heated at  $225^\circ$  until the weight is constant, then dissolved in water, and alcohol added, potassium dibromodi-isethionate is precipitated. *Potassium  $\alpha$ -bromo- $\beta$ -acetoxylethanesulphonate* crystallises in small, lustrous needles, is readily soluble in water, but only sparingly in boiling alcohol.

Phosphorus pentachloride converts potassium bromohydroxyethanesulphonate into an oil, probably the lactone,  $\text{O} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{array} \text{CHBr}$ , which slowly dissolves in cold water yielding bromohydroxyethanesulphonic acid. When the same potassium salt is suspended in chloroform and treated with phosphorus pentachloride,  $\beta$ -chlorobromethanesulphonic chloride,  $\text{C}_2\text{H}_3\text{ClBr} \cdot \text{SO}_2\text{Cl}$ , is obtained in the form of an oil, and this, when decomposed with water and neutralised with sodium hydroxide, yields the *sodium* salt,  $\text{C}_2\text{H}_3\text{ClBr} \cdot \text{SO}_3\text{Na}$ , which, on reduction with

zinc dust and water, yields sodium ethylenesulphonate. The constitution of bromohydroxyethanesulphonic acid follows from the fact that when reduced with dilute acid and sodium amalgam, isethionic acid (hydroxyethanesulphonic acid) is obtained; when oxidised with potassium permanganate, it yields carbonic anhydride, water, hydrogen bromide, and sulphuric acid, whilst with nitric acid, it yields oxalic acid; with silver oxide, glycollic acid; with barium manganate, *bromosulphoacetic acid*, the *barium* salt,  $C_2HBrO_5S_2Ba \cdot 2H_2O$ , of which crystallises in colourless needles.

*Potassium  $\alpha\beta$ -dibromethanesulphonate*, readily obtained when potassium bromethylenesulphonate is heated with fuming hydrobromic acid at  $120^\circ$  for 5 hours, crystallises in compact, lustrous prisms moderately soluble in cold water, but insoluble in alcohol; when reduced with zinc dust, ethylenesulphonic acid is formed, hence the two bromine atoms cannot be attached to the same carbon atom.

The nature of the products formed by the action of sulphuric acid on barium bromethylenesulphonate depends largely on the conditions. When the temperature is kept below  $80^\circ$  and only a slight excess of sulphuric acid is employed, the product is barium bromethionate, which, when boiled with water, yields barium sulphate and  $\alpha\beta$ -bromohydroxyethanesulphonic acid; if the temperature is raised to  $125^\circ$  for a few hours and an excess of acid employed, a sulphonic acid is obtained, the *barium* salt of which,  $(C_2H_2O_{10}BrS_3)_2Ba_3 \cdot 4H_2O$ , is sparingly soluble, crystallising in glistening plates; the acid is probably a bromine derivative of the compound obtained by Rathke (this Journal, 1872, 388) by the action of acid sulphites on chloral. When boiled with water, the barium salt is decomposed, yielding barium sulphite and *barium acetaldehydedisulphonate*,  $C_2HO_7BrS_2Ba \cdot 2H_2O$ ; the latter is decomposed by alkalis into barium formate and barium bromomethanedisulphonate,  $CHBrS_2O_6Ba$ .  
J. J. S.

**Oxidation of Alicyclic Compounds. Oxidation of Acetyltrimethylene.** By M. IDZKOWSKA and E. WAGNER (*Chem. Centr.*, 1898, ii, 474—475; from *J. Russ. Chem. Soc.*, 1898, 30, 259—269).—An almost quantitative yield of acetyltrimethylene may be obtained by Lipp's method (Abstr., 1889, 843) if an aqueous solution of potassium hydroxide is used. Acetyltrimethylene boils at  $113^\circ$  under 753.5 mm. pressure, and on oxidation in aqueous solution with potassium permanganate, loses carbonic anhydride, and forms trimethylenecarboxylic acid, which is isolated as an oil by acidifying the filtrate with phosphoric acid and distilling with steam. The residue contains a small quantity of an acid, which, with phenylhydrazine, forms yellowish crystals, and hence is a ketonic acid,

probably of the composition  $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} > CH \cdot CO \cdot COOH$ . The absence of formic, acetic, oxalic, malonic, and succinic acids proves that only acetyltrimethylene is formed from acetylpropylic bromide. The oxidation must take place directly without the intermediate formation of acetylpropylic alcohol, for neither acetopropionic nor acetic acid is found in the product.

In contrasting the oxidation of compounds containing open and closed chains, the authors point out that the methyl group of acetyltrimethylene is first oxidised, whilst in the case of methyl isopropyl ketone the CH-group is attacked, yielding acetic acid and acetone; the former instance shows that the carbon atom, combined with the smallest number of hydrogen atoms, resists oxidation best.

According to E. Wagner, the hydrocarbon obtained by Gustavson (Abstr., 1896, i, 669) from penterythritol cannot be vinyltrimethylene, since it yields neither acetyltrimethylene nor trimethylene-carboxylic acid. From its products of oxidation, it appears to be a mixture of methylenetetramethylene and cyclopentene. The formation of acetyltrimethylene is the first instance of transition from the fatty to the polymethylene series by simple elimination of hydrogen bromide. Wolf's *i*-angelicalactone is probably,  $\text{COMe} \cdot \text{CH} \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CH}_2 \end{array}$ .

E. W. W.

**Action of Hexachlorethane on Benzene in Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], 19, 554—556).—When finely powdered aluminium chloride is gradually added to a solution of hexachlorethane in benzene heated at 70—75° in a reflux apparatus, hydrogen chloride is evolved and the mixture darkens in colour, becoming finally quite black. After washing with water and potash, the liquid, on distillation, yields small quantities of chlorobenzene and anthracene, besides unaltered benzene and hexachlorethane. The behaviour of hexachlorethane in this reaction is precisely what would be expected from the compound  $\text{CHCl}_2 \cdot \text{CHCl}_2$ , a fact which is in keeping with the behaviour of other compounds, such as carbon tetrachloride and trichloroacetic chloride, in which carbon is united to four radicles of a negative character. N. L.

**Action of Pentachlorethane and of Tetrachlorethylene on Benzene in Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], 19, 557—559).—When finely powdered aluminium chloride is gradually added to a solution of pentachlorethane in benzene heated at 70°, the liquid blackens, hydrogen chloride is evolved, and on distillation of the washed product, triphenylmethane and anthracene are obtained. Anthracene alone is produced when tetrachlorethylene is substituted for pentachlorethane. N. L.

**Explanation of the Fittig Synthesis. III. Parabromotoluene and Sodium.** By MAX WEILER (*Ber.*, 1899, 32, 1056—1064. Compare Abstr., 1896, i, 237, 242).—Pure parabromotoluene was treated with sodium in toluene solution: 1600 grams yielded 145 grams of crude hydrocarbons boiling at 270—310°, from which about 50 grams of 4 : 4'-ditolyl were separated by repeatedly cooling and filtering, whilst 70 grams of an oil that would not crystallise remained; this boiled at 283—288°. Besides these, large quantities of toluene and hydrocarbons containing more than two tolyl residues were formed.

The oil was oxidised repeatedly with chromic acid, the acids formed

and the ketones being removed each time, whilst the remaining neutral liquid was again submitted to oxidation. The ketones consisted of phenyl paratolyl ketone and another, or others, not isolated. The acids were separated by means of the difference (a) in volatility with steam of themselves or their methylic salts, and (b) in solubility of their barium salts; oxidation with alkaline permanganate being also employed. Those isolated were benzoic, terephthalic, isophthalic, and 4:4', 4:3', and perhaps traces of 3:3'-diphenyldicarboxylic acids. The original mixture of hydrocarbons must therefore have contained 4:4'- and 4:3'- (and 3:3'-?) ditolyl and 4-tolylphenylmethane; also dibenzyl, for some of this was left when a portion of the mixture was oxidised with chromyl chloride in carbon bisulphide solution (compare this vol., i, 519), and it is known that dibenzyl is attacked less readily than its isomerides under these circumstances. In the synthesis, the hydrocarbons were formed in about the following proportions:—Ditolyl: 4:4'—about 43 per cent.; 4:3', 6.5 per cent. or more; dibenzyl, about 2.5 per cent.; 4-tolylphenylmethane, 1 per cent. or more. The 4-bromotoluene had thus reacted as if it contained 3'-bromotoluene and benzylic bromide, although a pure substance was actually employed.

*Diphenyl-4:3'-dicarboxylic acid* was present amongst the acids not volatile with steam; these were converted into methylic salts, which were then treated with phenylhydrazine (to render non-volatile the methylic salts of any ketonic acids) and distilled with steam; the volatile portion was cooled, filtered from the methylic terephthalate that separated, and converted into barium salts, which were then crystallised fractionally; the acids from the less soluble fraction were oxidised with alkaline permanganate, and crystallisation of the barium salts was again employed; the more soluble salt was that of the acid in question, the less soluble being that of the 4:4'-isomeride. *Diphenyl-4:3'-dicarboxylic acid* melts at 333.5—334.5°, and its *dimethylic* salt at 98.5—99.5°; when oxidised with chromic acid in boiling acetic acid solution, it yields mainly terephthalic and some isophthalic acid.

*Dimethylic ditolyl-4:4'-dicarboxylate* was prepared incidentally, and for the first time, by treatment of the acid with phosphorus pentachloride and methylic alcohol; it melts at 212—213°.

C. F. B.

**Homologous Hydrocarbons of the Mesitylene Type.** By LUDWIG GATTERMANN, SIGM. FRITZ, and K. BECK (*Ber.*, 1899, 32, 1122—1127).—1:3:5-Triethylbenzene is best prepared by passing dry ethylene during 3—4 hours into a mixture of benzene and aluminium chloride heated on the water-bath in a reflux apparatus, and subsequently pouring on to powdered ice and fractionally distilling the product; the portion boiling between 200—215° consists of the nearly pure hydrocarbon. *Symmetrical triethylbenzamide*,  $C_6H_2Et_3 \cdot CO \cdot NH_2$ , prepared by the cyanuric acid method (this vol., i, 509), or, better, by gradually adding, at 0°, finely powdered aluminium chloride to a solution of 1:3:5-triethylbenzene and chloroformamide in carbon bisulphide, crystallises from light petroleum in colourless needles, melts at 155—156°, and is not changed by heating during several days with alcoholic potash; it is easily hydrolysed, however, by treatment with

nitrous acid (*loc. cit.*), giving rise to 2:4:6-triethylbenzoic acid, which crystallises from light petroleum in colourless, highly-refracting, monoclinic plates, melts at  $113^{\circ}$ , and yields no trace of the ethylic salt when heated for 4 hours on the water-bath with 3 per cent. alcoholic hydrogen chloride. The influence of a contiguous ethyl group in preventing etherification is thus the same as that of methyl in the cases studied by Victor Meyer and Sudborough. Pure 1:3:5-triethylbenzene, prepared from its carboxylic acid, boils at  $218^{\circ}$  and yields a dinitro-derivative,  $C_{13}H_{16}N_2O_6$ , which crystallises from light petroleum in short, yellow needles, and melts at  $128-129^{\circ}$ ; *symmetrical tribromotriethylbenzene*,  $C_{12}H_{15}Br_3$ , separates from absolute alcohol in stout, colourless crystals and melts at  $105-106^{\circ}$ , whilst *symmetrical trinitrotriethylbenzene*,  $C_{12}H_{15}N_3O_6$ , forms silky, yellow needles, and melts and decomposes at  $108-109^{\circ}$ . *Diacetyltriethylbenzene*,  $C_{16}H_{22}O_2$ , prepared by warming at  $30-40^{\circ}$  a mixture of the hydrocarbon with acetic chloride, carbon bisulphide, and finely powdered aluminium chloride, separates from light petroleum in highly refracting, colourless crystals, and melts at  $77^{\circ}$ .

Symmetrical methyldiethylbenzene is conveniently prepared by passing ethylene into toluene in presence of aluminium chloride; the *methyldiethylbenzamide*,  $C_{12}H_{17}NO$ , obtained from it, crystallises from light petroleum in slender, colourless needles, melts at  $106-107^{\circ}$ , and, on hydrolysis with nitrous acid, yields the *acid*,  $C_{12}H_{16}O_2$ , which forms stout crystals, melts at  $90-91^{\circ}$ , and yields only traces of the ethereal salt when subjected to E. Fischer's etherification process; *trinitromethyldiethylbenzene*,  $C_{12}H_{15}N_3O_6$ , crystallises in yellow leaflets and melts at  $86-87^{\circ}$ .

1:3:5-Dimethylethylbenzene, prepared by passing ethylene into metaxylene containing aluminium chloride, boils at  $185-195^{\circ}$ , and yields a *dimethylethylbenzoic acid*,  $C_6H_2Me_2Et\cdot COOH$ , which crystallises from light petroleum in measurable crystals, melts at  $101^{\circ}$ , and does not form an ethereal salt when treated by Fischer's method; the *amide*,  $C_6H_2Me_2Et\cdot CO\cdot NH_2$ , forms colourless needles, and melts at  $87.5^{\circ}$ , whilst the *dinitro-derivative*,  $C_{11}H_{12}N_2O_6$ , crystallises from alcohol in yellow plates and melts at  $154^{\circ}$ .

W. A. D.

**Phenylic Alkyl Phosphates.** By ALBERT MOREL (*Compt rend*, 1899, 128, 507-510. Compare this vol., i, 29, 264).—When triphenylic phosphate is treated in presence of alcohol and ether with one mol. of sodium ethoxide, it yields diphenylic ethylic phosphate; with two molecular proportions, phenylic diethyl phosphate, and with three, diethyl sodium phosphate, phenylic ethylic ether, and sodium phenoxide.

The action of sodium ethoxide (1 mol.) on diphenylic ethylic phosphate (1 mol.) yields phenylic diethyl phosphate; that of sodium propoxide (1 mol.) yields phenylic ethylic propylic phosphate. The action of sodium ethoxide (2 mols.), however, does not yield triethyl phosphate, but diethyl phosphate and phenylic ethylic ether.

Triphenylic phosphate is not affected when boiled for a long time with alcohol or with alcoholic solutions of carbamide, quinoline, or pyridine.

A boiling solution of dimethylpiperazine in dilute alcohol converts triphenylic phosphate into diphenylic ethylic phosphate, but after prolonged boiling, or with a large excess of the base, the product is dimethylpiperazine phosphate.

The reaction with sodium ethoxide affords further illustration of the difference between the function of one hydroxyl of phosphoric acid and that of the other two, whilst dimethylpiperazine distinguishes between the two hydroxyls which behave similarly with sodium ethoxide. C. H. B.

**Nitroquinone.** By FRIEDRICH KEHRMANN and M. IDZKOWSKA (*Ber.*, 1899, 32, 1065—1072).—In the preparation of orthonitroparamidophenol by the action of sulphuric acid on metanitrodiazobenzeneimide (Friedländer and Zeitlin, *Abstr.*, 1894, i, 185), some of the 4:2-isomeride is formed, and remains in the mother liquor of the first substance. The oxidation of that substance does not yield 2-nitro-1:4-quinone (*Abstr.*, 1895, i, 186); the product is in reality a substituted anilide of this,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OH}$  [ $\text{NH}:\text{NO}_2:\text{O}_2 = 1:3:2:5$  or  $1:2:3:6$ ;  $\text{NH}:\text{NO}_2:\text{OH} = 1':3':4'$ ]. When heated with aniline, it undergoes a gradual transformation through the compound  $\text{NO}_2 \cdot \text{C}_6\text{HO}_2(\text{NHPh}) \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{OH}$  [ $\text{NHPh} = 4$ ] into the dianilidonitroquinone,  $\text{NO}_2 \cdot \text{C}_6\text{HO}_2(\text{NHPh})_2$ , phenol being set free; the dianilido-compound is obtained pure only after prolonged treatment with aniline. When it is heated in acetic acid solution with fuming hydrochloric acid at the ordinary temperature, and the product oxidised with chromic acid, a dark brown *chloroquinone*,  $\text{C}_{12}\text{H}_6\text{ClN}_3\text{O}_7$ , is obtained. The dianilidonitroquinone is certainly a paradianilido-compound, for it is formed in small amount, together with much blue *nitranilidohydroxyquinoneanilide*,  $\text{NHPh} \cdot \text{C}_6\text{HO}(\text{NO}_2)(\text{OH}) \cdot \text{NPh}$  [ $1:2:6:4:5$ ], when the aniline salt of nitroparahydroxyquinone (Nietzki and Schmidt, *Abstr.*, 1889, 968) is boiled with excess of aniline. C. F. B.

**Ethanecatechol [Catechol Ethylenic Ether] and its Derivatives.** By CHARLES MOUREU (*Bull. Soc. Chim.*, 1898, 19, [iii], 507—511. Compare *Abstr.*, 1898, i, 660, and this vol., i, 125).—The

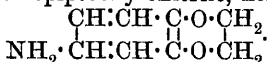
*alcohol*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{smallmatrix}$  obtained by treating catechol with dibromohydrin in the presence of alkalis, crystallises in white needles, melts at 89—90°, and boils at 283—286°. The corresponding *acetate* boils at 185—188° under 30 mm. pressure.

*Ethane protocatechuic aldehyde (homopiperonal)*, produced by the action of ethylenic dibromide on the disodium derivative of protocatechuic aldehyde, crystallises in silky needles, melts at 50—51.5°, and boils at 299°. The name homopiperonal is given to this substance on account of its relationship to piperonal, and from its mode of formation it must be represented by the formula

$\text{COH} \cdot \text{C} \begin{smallmatrix} \text{CH}:\text{CH} \cdot \text{C} \cdot \text{O} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C}=\text{CH} \cdot \text{C} \cdot \text{O} \cdot \text{CH}_2 \end{smallmatrix}$ ; the constitution of the related compounds being deduced from it. The *phenylhydrazone* of homopiperonal melts at 107—108°. The *aldoxime*

melts at 75—75.5°, and can be converted into *homopiperonylonitrile*, which crystallises in white needles and melts at 105°.

The nitro-derivative of catechol ethylenic ether, obtained by Vorländer (Abstr., 1895, i, 19), yields *amidocatechol ethylenic ether*, a heavy oil boiling at 162° under 9 mm. pressure; the *hydrochloride* decomposes at 220°, the *picrate* at 180°, and the *platinochloride* at 213°. When this amine is diazotised and treated with cuprous cyanide, it yields homopiperonylonitrile, hence the base has the following constitution:



*Homopiperonylic acid*, obtained by hydrolysing the nitrile with alcoholic potash, melts at 137°. G. T. M.

**Ethylenecatechol [Catechol Acetylenic Ether].** By CHARLES MOUREU (*Compt. rend.*, 1899, 128, 559—561).—Catechol acetylenic ether,

$\text{C}_6\text{H}_4\begin{array}{c} \text{O}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CH} \end{array}$ , obtained in small quantity by the action of acetic chloride on orthohydroxyphenoxyacetal, or on ethoxyethanecatechol, is readily prepared by dehydrating orthohydroxyphenoxyaldehyde with phosphoric anhydride in presence of quinoline. It is a colourless, neutral, oily liquid which boils at 76° under 13 mm. pressure and at 193° (corr.) under normal pressure, and has a sp. gr. 1.204 at 0°. When strongly cooled, it forms brilliant, white leaflets which melt between 16° and 20°. In presence of carbon bisulphide, it combines readily with bromine, without production of hydrogen bromide, and yields the dibromide,  $\text{C}_6\text{H}_4\begin{array}{c} \text{O}\cdot\text{CHBr} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CHBr} \end{array}$ , which crystallises from light petroleum in small, colourless prisms melting at 103—104.5°. In contact with hot water, this dibromide is converted into catechol, glyoxal, and hydrogen bromide. This reaction establishes the constitution of catechol acetylenic ether, which affords the first example of an unsaturated hexagonal nucleus containing two atoms of oxygen. C. H. B.

**Methylethylenecatechol [Catechol Methylacetylenic Ether].** By CHARLES MOUREU (*Compt. rend.*, 1899, 128, 670—673. Compare Abstr., 1898, i, 644, 660; and this vol., i, 125, 138, 433, and preceding abstract).

—*Catechol methylacetylenic ether*,  $\text{C}_6\text{H}_4\begin{array}{c} \text{O}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CMe} \end{array}$ , produced either by dehydrating 1-hydroxy-2-phenoxyacetone,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{COMe}$ , with phosphoric anhydride or by treating it with acetic chloride in the presence of ethylic orthoformate, is an oil distilling between 97° and 102° under 18 mm. pressure, or between 213° and 218° under ordinary pressures, and has a sp. gr. 1.1593 at 0°. It forms an unstable dibromide when treated with a cold solution of bromine in chloroform; the additive product, when boiled with water, decomposes, yielding catechol and hydrogen bromide; methylglyoxal, which should also result from this hydrolysis, could not be detected. G. T. M.

**Synthesis of Estragole and of Allylic Compounds.** By CHARLES MOUREU (*Bull. Soc. Chim.*, 1898, [iii], 19, 399—403).—A number of unsuccessful attempts were made to prepare estragole (paramethoxy-



allylbenzene) by heating a mixture of allylic iodide and anisoil with zinc powder, and by the action of allylic chloride, bromide, or iodide on pariodanisoil or parabromanisoil in the presence of sodium and anhydrous ether. A vigorous and complex reaction occurs in each case, but estragole appears not to be formed. Estragole is probably produced when allylic chloride is gradually added to a solution of aluminium chloride in excess of anisoil, but in too small a quantity to admit of separation and identification. The chief product of the reaction is *dianisylpropane*,  $C_3H_6(C_6H_4 \cdot OMe)_2$ , a white, odourless, crystalline solid which melts at  $68-69^\circ$ , boils at about  $200^\circ$  under 10 mm. pressure, and yields paramethoxybenzoic acid on oxidation with dilute nitric acid. This compound is evidently formed by the action of the estragole first produced on the excess of anisoil present, possibly with the intermediate formation of chloropropylanisoil. It seems probable that the synthesis of estragole might be effected by the action of sodium allyloxide on sodium paramethoxybenzenesulphonate or on the corresponding sulphinate. Anisoil and phenetoil are readily obtained by distilling a mixture in molecular proportion of sodium benzenesulphonate with sodium methoxide and ethoxide respectively, but experiments with sodium benzenesulphinate seem to show that the use of this substance is impracticable.

N. L.

**Oxidation of Organic Bases with Hydrogen Peroxide.** By RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 688—689).—Surprise is expressed that Bamberger and Tschirner (this vol., i, 348) should have investigated the action of hydrogen peroxide on tertiary bases, as this forms a natural continuation of the work of Wernick and the author (*Abstr.*, 1898, i, 536).

C. F. B.

**Oxidation of Aromatic Bases.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1159—1161).—A reply to Wolfenstein (preceding abstract).

W. A. D

**Derivatives of Paramidophenol.** By OSCAR HINSBERG (*Annalen*, 1899, 305, 276—289).—*N-Methylphenacetin*,  $OEt \cdot C_6H_4 \cdot NMeAc$ , prepared by adding slight excess of methylic iodide to xylene in which the sodium derivative of phenacetin is suspended, separates from light petroleum in colourless crystals and melts at  $41^\circ$ ; contact with water transforms it into an oil which dissolves in a large proportion of water. It is noteworthy that the narcotic action of phenacetin is considerably increased by introducing the methyl group.

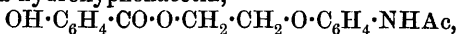
*N-Ethylphenacetin*,  $OEt \cdot C_6H_4 \cdot NEtAc$ , melts at  $38^\circ$ , and resembles the methylic derivative in taste and odour; it is a more powerful narcotic than the foregoing substance.

*N-Isopropylphenacetin*,  $OEt \cdot C_6H_4 \cdot NPr^sAc$ , is a colourless, viscous oil, readily soluble in alcohol, ether, and benzene, and dissolving also in 260 parts of water at  $30^\circ$ . The narcotic action of isopropylphenacetin and the higher homologues is less powerful than that of the methylic and ethylic derivatives.

*Acetamidophenylic propylic ether*,  $OPr^a \cdot C_6H_4 \cdot NHAc$ , prepared from acetamidophenol, alcoholic soda, and propylic iodide, crystallises from

dilute alcohol in colourless leaflets, and melts at  $122^{\circ}$ ; as a febrifuge, its action is feeble than that of phenacetin.

*ω*-Bromophenacetin,  $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , obtained by heating acetamidophenol with ethylenic bromide and caustic soda, crystallises from dilute alcohol in white needles and melts at  $130^{\circ}$ . When heated with sodium salicylate at  $160$ — $180^{\circ}$ , it yields the *salicylic* derivative of *ω*-hydroxyphenacetin,

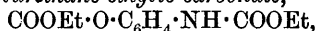


which crystallises from alcohol, and melts at  $133^{\circ}$ .

*Acetamidophenylic ethylic carbonate*,  $\text{COOEt}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$ , prepared from acetamidophenol, caustic soda, and ethylic chlorocarbonate, crystallises from dilute alcohol in colourless needles and melts at  $121^{\circ}$ .

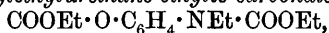
*N*-Ethylacetamidophenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NEtAc}$ , crystallises from alcohol in colourless needles and melts at  $187^{\circ}$ ; the *acetyl* derivative crystallises from light petroleum or ether, and melts at  $58^{\circ}$ . The ethylamidophenol from which ethylacetamidophenol is prepared can be obtained by the action of concentrated hydrochloric acid on ethylphenacetin at  $220$ — $240^{\circ}$ , and also by gently heating paramidophenol in alcoholic solution with ethylic bromide (1 mol.).

*Parahydroxyphenylethylurethane ethylic carbonate*,



produced by the action of ethylic chlorocarbonate on paramidophenol in dilute caustic soda, crystallises from dilute alcohol in colourless needles and melts at  $108$ — $109^{\circ}$ .

*Parahydroxyphenylethylurethane ethylic carbonate*,



prepared from ethylparamidophenol and ethylic chlorocarbonate, separates from dilute alcohol in colourless crystals and melts at  $60$ — $62^{\circ}$ .

*Paramidophenylic hydrogen tartrate* separates from water in large, transparent crystals, and decomposes at  $216^{\circ}$ . M. O. F.

**1 : 3 : 2-Metaxyridine.** By MAX BUSCH (*Ber.*, 1899, 32, 1008—1012). —*Formylmetaxyridide* [ $\text{Me}_2\text{:NH}\cdot\text{CHO}=1:3:2$ ] crystallises from alcohol in white, silky needles and melts at  $159$ — $160^{\circ}$ . *1 : 3 : 2-Benzylidenemetaxyridine* is a yellow oil; its formation takes place more slowly than in those cases where the ortho-positions are occupied by hydrogen. *Metanitrobenzylidene-1 : 3 : 2-metaxyridine* separates from alcohol in yellow crystals and melts at  $105^{\circ}$ ; the *orthonitro*-compound forms reddish-brown crystals. *Orthohydroxybenzylidene-1 : 3 : 2-metaxyridine* is a yellow oil. *Disylylthiocarbamide*,  $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_5)_2$ , crystallises from alcohol in transparent prisms and melts at  $231^{\circ}$ . *Xylylthiocarbimide* is a thick, transparent oil which solidifies to flaky crystals and melts at the temperature of the hand; it behaves in the normal way towards amines and hydrazines. *Phenylxylylthiocarbamide* crystallises from alcohol in slender, white needles, dissolves most readily in boiling acetic acid, and melts at  $204^{\circ}$ . *1-Phenyl-4-xylylthiosemicarbazide*,  $\text{NHPh}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , separates from alcohol in colourless crystals, and melts and decomposes at  $210^{\circ}$ .

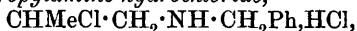
*1 : 3 : 2-Xylylhydrazine* crystallises from light petroleum in glisten-

ing, white needles, and melts at  $46^{\circ}$ ; it decomposes gradually, forming a brown oil. *Benzylidenexylylhydrazine* is an unstable, yellow oil. *Metanitrobenzylidenexylylhydrazine* separates from alcohol in orange-coloured needles and melts at  $119$ — $120^{\circ}$ . *4-Phenyl-1-xyllylthiosemicarbazide*,  $C_8H_9 \cdot NH \cdot NH \cdot CS \cdot NHPh$ , forms glistening, white needles, melts at  $181$ — $182^{\circ}$ , and is insoluble in ether and benzene, but dissolves slightly in alcohol, and more readily in boiling acetic acid. T. M. L.

**Derivatives of  $\beta$ -Bromopropylamine.** By AUGUST UEDINCK (*Ber.*, 1899, 32, 967—979).— $\beta$ -Bromopropylbenzamide is obtained when  $\beta$ -bromopropylamine hydrobromide is treated with benzoic chloride by the Schotten-Baumann method.  $\mu$ -Phenyl- $\beta$ -methyl-oxazoline (*Abstr.*, 1891, 1267) may be obtained by mixing the amide with boiling water and potassium hydroxide, and immediately distilling in a current of steam; the yield is 60—66 per cent. of the theoretical. From the residue,  $\beta$ -hydroxypropylbenzamide (*Abstr.*, 1891, 860) may be obtained by evaporation.

*Benzyl- $\beta$ -hydroxypropylamine*,  $OH \cdot CHMe \cdot CH_2 \cdot NH \cdot CH_2Ph$ , is formed when the oxazoline is reduced with sodium and ethylic alcohol, the alcohol and unaltered oxazoline removed by distillation in steam, and the base purified by solution in oxalic acid and subsequent distillation under diminished pressure; it is a thick, colourless, strongly refractive liquid which boils at  $136$ — $140^{\circ}$ ,  $143$ — $146^{\circ}$ ,  $147$ — $149^{\circ}$ , and  $151$ — $154^{\circ}$  under pressures of 7, 13, 15, and 19 mm. respectively, has a sp. gr.  $1.84$  at  $17.5^{\circ}/4^{\circ}$ , is moderately soluble in water, yielding a strongly alkaline solution, and absorbs both moisture and carbonic anhydride from the atmosphere. Its *hydrochloride* crystallises in thin, rectangular plates melting at  $119$ — $120^{\circ}$ , and readily soluble in alcohol, chloroform, or water; its *hydrobromide* in glistening plates melting at  $122^{\circ}$ , and its *hydriodide* at  $119^{\circ}$ . The *picrate*,  $C_{10}H_{15}NO, C_6H_3N_3O_7$ , forms small plates melting at  $127$ — $128^{\circ}$ ; the *platinochloride* crystallises in dark red, rhombic plates melting and decomposing at  $185^{\circ}$ ; the *aurichloride* forms small, yellow plates melting at  $114^{\circ}$ , and the *nitrosamine*,  $C_{10}H_{14}ON \cdot NO$ , is a dark yellow oil.

*Benzyl- $\beta$ -chloropropylamine hydrochloride*,



is obtained when benzyl- $\beta$ -hydroxypropylamine hydrochloride is heated with an excess of the strongest hydrochloric acid for 8 days at  $100^{\circ}$ ; after purification by solution in absolute alcohol and precipitation with ether, it forms small, glistening scales melting at  $158$ — $159^{\circ}$ . The *picrate* crystallises in small, yellow, lozenge-shaped plates. *Benzyl- $\beta$ -iodopropylamine hydriodide* crystallises from hot water in colourless, rectangular plates melting at  $168$ — $169^{\circ}$ , and yields a *picrate* melting at  $111$ — $112^{\circ}$ . *Benzyl- $\beta$ -bromopropylamine hydrobromide* crystallises in colourless scales, melts at  $170$ — $171^{\circ}$ , and yields a *picrate* crystallising in yellow needles and melting at  $125$ — $126^{\circ}$ .

*Dibenzyl-dimethylpiperazine*,  $CH_2Ph \cdot N \begin{smallmatrix} \text{CH}_2 \cdot CHMe \\ CHMe \cdot CH_2 \end{smallmatrix} N \cdot CH_2Ph$ ,

may be isolated from the brown residue obtained when the last hydrobromide is treated with potassium hydroxide and immediately distilled

in steam; it crystallises from ether in thin, transparent, rhombic plates melting at 105—106°, and yields sparingly soluble salts. The yield of base is poor, as the alkali converts part of the  $\beta$ -bromo-compound into benzyl- $\beta$ -hydroxypropylamine.

The compound formerly described as *n*-benzylethylene- $\psi$ -thiocarbamide (Abstr., 1896, i, 702) should be  $\nu$ -benzylethylene- $\psi$ -thiocarb-

amide,  $\begin{array}{c} \text{CH}_2\text{---S} \\ | \\ \text{CH}_2\cdot\text{N}(\text{C}_7\text{H}_7) \end{array} > \text{C:NH}$ ; the corresponding *propylene* derivative,

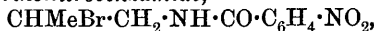
$\begin{array}{c} \text{CHMe---S} \\ | \\ \text{CH}_2\cdot\text{N}(\text{C}_7\text{H}_7) \end{array} > \text{C:NH}$ , is obtained in the form of its *thiocyanate* by

the action of potassium thiocyanate on  $\beta$ -bromopropylbenzylamine hydrobromide; the salt crystallises in tufts of needles melting at 126—127°. The *base* is a thick, yellow oil of alkaline reaction and readily soluble in the usual organic solvents. The *hydrochloride* crystallises in glistening, rhombic plates melting at 215—216°, the *aurichloride* in lemon-yellow needles melting and decomposing at 146—148°, the *platinochloride* in short, orange-red prisms melting and decomposing at 216—218°, and the *picrate* in dark yellow needles melting at 117—119°. When oxidised by Andreasch's method, (Abstr., 1883, 664), the base yields a compound,  $\text{C}_{11}\text{H}_{13}\text{N}_2\text{ClSO}_2$ , crystallising in colourless needles and melting at 125—126°, to which

the authors assign the constitution  $\begin{array}{c} \text{CHMe---SO}_2 \\ | \\ \text{CH}_2\cdot\text{N}(\text{CH}_2\text{Et}) \end{array} > \text{C:NCl}$ .

$\beta\mu$ -Dimethyloxazoline,  $\begin{array}{c} \text{CHMe}\cdot\text{O} \\ | \\ \text{CH}_2\text{---N} \end{array} > \text{CMe}$ , obtained when  $\beta$ -bromopropylamine hydrobromide is boiled for 3 hours with three times its weight of acetic anhydride, forms a mobile liquid boiling at 117—119°. The *picrate* melts at 114—115°, the *platinochloride* forms orange-yellow needles, readily soluble in water, and melting and decomposing at 188—190°. When an aqueous solution of the hydrochloride of the base is heated, hydrolysis ensues and  $\beta$ -amidoisopropylacetic acid,  $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NH}_2$ , is obtained as a clear syrup, which yields a *platinochloride* melting and decomposing at 207—209°.

$\beta$ -Bromopropylorthonitrobenzamide,



obtained by the action of orthonitrobenzoic chloride on  $\beta$ -bromopropylamine hydrobromide, crystallises from benzene in long needles melting at 104—105°, and when treated according to Elfeldt's method (Abstr., 1892, 213), yields  $\mu$ -orthonitrophenyl- $\beta$ -methyloxazoline,  $\begin{array}{c} \text{CHMe}\cdot\text{O} \\ | \\ \text{CH}_2\text{---N} \end{array} > \text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , as a colourless liquid with a pleasant odour, distilling at 173—176° under 8 mm. pressure. The *hydrochloride*,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_3\cdot\text{HCl}$ , crystallises in long, slender needles melting at 119—120°; the *picrate* in yellow needles melting at 129—130°, and the *platinochloride* in dark orange-yellow needles melting and decomposing at 187—188°.

*Amidoisopropyl orthonitrobenzoate* yields a *platinochloride* which crystallises in short, pale orange-yellow needles melting and decomposing at 215°, and a *picrate* melting at 176—178°.  $\beta$ -Bromopropylparanitro-

*benzamide* crystallises from benzene or absolute alcohol in greenish-yellow needles melting at  $135^{\circ}$ .  *$\mu$ -Paranitrophenyl- $\beta$ -methyloxazoline* crystallises from 70 per cent. alcohol in thin, rectangular plates melting at  $134$ – $135^{\circ}$ ; it yields a *platinochloride*, crystallising in dark reddish-yellow needles melting and decomposing at  $192^{\circ}$ , and a *picrate* melting at  $185$ – $186^{\circ}$ . *Amidoisopropyllic paranitrobenzoate* crystallises from hot water in glistening scales, melting at  $167$ – $168^{\circ}$ ; its *hydrochloride* melts at  $191$ – $192^{\circ}$ , its *platinochloride* melts and decomposes at  $191$ – $193^{\circ}$ , and its *picrate* melts at  $168$ – $169^{\circ}$ . J. J. S.

**Paradihydroxydiphenylamine.** By FELIX SCHNEIDER (*Ber.*, 1899, 32, 689–691).—*Paradihydroxydiphenylamine*,  $\text{NH}(\text{C}_6\text{H}_4\cdot\text{OH})_2$ , is obtained by heating quinol with ammonium chloride and caustic soda for seven hours, first at  $160^{\circ}$ , then at  $180^{\circ}$ ; or by heating quinol with paramidophenol and fused calcium chloride for 5 hours at  $160$ – $180^{\circ}$ . In the first case, the product is boiled with 1 per cent. hydrochloric acid, the solution is filtered, unchanged quinol is removed by extraction with ether, and then the base is precipitated by the addition of sodium acetate. In the second case, the product is dissolved in water, the solution decolorised by the addition of a few drops of hydrochloric acid, boiled, filtered, and set aside to crystallise. In both cases, the crude product is recrystallised from water. It melts at  $174.5^{\circ}$ , gives a blue solution in concentrated sulphuric acid, changing to brown when diluted, dissolves in acids and in alkalis with a blue colour, doubtless owing to oxidation to indophenol,  $\text{O}:\text{C}_6\text{H}_4:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , of which it is the leuco-compound; it is also oxidised to this substance in benzene solution by mercuric oxide. It forms a *triacetyl* derivative melting at  $128.5^{\circ}$ .

From quinol and paraphenylenediamine, in the presence of dehydrating agents, a *compound*, apparently  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}\cdot 2\text{HCl}$ , was eventually obtained; it melted and decomposed above  $190^{\circ}$ .

C. F. B.

**Formation of Dimethylaniline by the Action of Bromo- or Iodo-benzene and Phenol on Dimethylamine.** By BORIS N. MENSCHUTKIN (*Chem. Centr.*, 1898, ii, 478–479; from *J. Russ. Chem. Soc.*, 1898, 30, 243–251).—When bromo- or iodo-benzene is heated with dimethylamine at  $250$ – $260^{\circ}$  for 5–6 days, the product contains dimethylaniline; this is also obtained by heating phenol with dimethylamine at  $250^{\circ}$  for 60–84 hours. By adding potassium hydroxide to the product after all the free dimethylamine has been removed, a further quantity of dimethylamine is formed, probably owing to the decomposition of a phenolate of the amine  $\text{NHMe}_2\cdot\text{PhOH}$ .

An almost theoretical yield of dimethylamine hydrochloride is obtained by adding powdered nitrosodimethylaniline hydrochloride and a few zinc shavings to a nearly boiling, dilute aqueous solution of sodium hydroxide; the amine is absorbed in a Pélignet's U-tube containing concentrated hydrochloric acid. E. W. W.

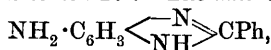
**Salts of Methyl- and Dimethyl-aniline with Halogen Acids.** By BORIS N. MENSCHUTKIN (*Chem. Centr.*, 1898, ii, 479; from *J. Russ. Chem. Soc.*, 1898, 30, 251–259).—Dimethylaniline hydrochloride

prepared from dry hydrogen chloride and dimethylaniline, can be purified by freezing in benzene solution; it separates from benzene in white, crystalline flakes melting at  $85^{\circ}$ , but can be crystallised from aqueous solution in long, thin plates melting at  $80-81^{\circ}$ . The hydrobromide melts at  $75^{\circ}$ . The hydriodide, prepared from dry hydrogen iodide and commercial dimethylaniline and washed with benzene, in which it is insoluble, melts at  $112^{\circ}$  and forms crystals which are affected by light; it separates from water in white crystals, like octahedra, and then melts at  $111^{\circ}$ . Pure dimethylaniline is best prepared from this salt; it melts at  $2.5^{\circ}$ , boils at  $192.5^{\circ}$  under 761 mm. pressure, and has a sp. gr. 0.9580 at  $18^{\circ}$ .

Methylaniline hydrochloride, prepared like the corresponding dimethylaniline salt, separates in white crystals, melts at  $121-122^{\circ}$ , is not hygroscopic, and is insoluble in benzene. The hydrobromide melts at  $98^{\circ}$ . The hydriodide separates in crystals, melts at  $124^{\circ}$ , and is insoluble in benzene.

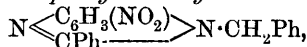
Hydrogen bromide can be prepared by adding bromine to a cold mixture of iron powder (*ferrum alcoholisatum*), copper sulphate, and benzene. E. W. W.

**Amido-amidines. IV.** By FERNAND MUTTELET (*Bull. Soc. Chim.*, 1898, 19, [iii], 519—520. Compare this vol., i, 354).—Benzo-dinitranilide, obtained by heating dinitraniline [ $\text{NH}_2:\text{NO}_2:\text{NO}_2 = 1:2:4$ ] with benzoic chloride at  $170-180^{\circ}$ , separates from hot toluene in yellow, granular crystals and melts at  $220^{\circ}$ . The *amido-amidine*,



produced by reducing the preceding compound, crystallises from dilute alcohol in pink granules and melts at  $286-288^{\circ}$ ; it is isomeric with an amidine obtained by Lauth (*Abstr.*, 1897, i, 516). G. T. M.

**Substantive Azo-dyes of the Benzimidazole Series.** By JOHANNES PINNOW and F. WISKOTT (*Ber.*, 1899, 32, 898—915).—Nitro-orthophenylenediamine reacts with benzaldehyde in alcoholic solution forming two compounds. *Benzenylnitrophenyleneamidine* (3-nitro-2'-phenylbenzimidazole,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{CPh}$ , is soluble in potash, and crystallises in almost colourless needles melting at  $203^{\circ}$ . *Nitrobenzaldehydine* (3-nitro-2'-phenyl-1'-benzylbenzimidazole),



is insoluble in potash and crystallises in light yellow needles melting at  $187-188^{\circ}$ ; two isomeric forms of this compound are probably produced. *Amidobenzaldehydine* is formed by the reduction of the nitro-compound and crystallises in colourless prisms melting at  $192^{\circ}$  (Hinsberg's compound melted at  $121^{\circ}$ ; *Abstr.*, 1896, i, 537). The *hydrobromide* crystallises with  $5\text{H}_2\text{O}$ , the *picrate* melts at  $231^{\circ}$ , and the *acetyl* derivative at  $214^{\circ}$ . The base is readily converted into a diazo-salt which reacts with phenol to form *benzaldehydine-azophenol*,  $\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}$ , a yellow, crystalline powder melting at  $273^{\circ}$ . Benzenylamidophenyleneamidine (2'-phenylamidobenzimidazole) crystallises in plates, which do not melt below  $280^{\circ}$ , and has been obtained by

Muttele (preceding abstract) by the reduction of benzo- $\alpha$ -dinitranilide. The *hydrobromide* crystallises in prisms, the *picrate* melts at  $220^{\circ}$ , and the *acetyl* derivative at  $241^{\circ}$ . The base readily yields colouring matters, such as *phenylbenzimidazoleazodimethylaniline*, a yellow, crystalline powder melting at  $268^{\circ}$ .

Orthophenylenediamine reacts with metanitrobenzaldehyde forming *nitrobenzenylphenyleneamidine* (metanitro-2'-phenylbenzimidazole)  $C_{13}H_9N_3O_2$ , which crystallises in needles or prisms melting at  $204$ – $205^{\circ}$ . 2'-Nitrophenyl-1'-nitrobenzylbenzimidazole is also formed in this reaction and crystallises in prisms or pyramids melting at  $170$ – $171^{\circ}$ . *Amidobenzenylphenyleneamidine* crystallises in needles decomposing at  $220^{\circ}$ , and yields an *acetyl* derivative decomposing at  $250^{\circ}$ . The base readily yields colouring matters with metaphenylenediamine and with  $\alpha$ -naphthol. *Diamidobenzenaldehyde* crystallises in prisms melting at  $194^{\circ}$ , and forms a *diacetyl* derivative melting at  $219^{\circ}$ . Both the amido-groups undergo the diazo-reaction readily. When treated with metanitrobenzaldehyde, nitro-orthophenylenediamine yields *trinitrobenzaldehyde* (1'-nitrobenzyl-2'-nitrophenyl-3-nitrobenzimidazole),  $N \left\langle \begin{smallmatrix} C_6H_3(NO_2) \\ C(C_6H_4 \cdot NO_2) \end{smallmatrix} \right\rangle N \cdot CH_2 \cdot C_6H_4 \cdot NO_2$ , melting at  $236^{\circ}$ , along with *nitrobenzenylnitrophenyleneamidine* (2'-nitrophenyl-3-nitrobenzimidazole),  $NO_2 \cdot C_6H_3 \left\langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \right\rangle C \cdot C_6H_4 \cdot NO_2$ , which melts at  $283^{\circ}$  and is soluble in alkalis. *Triamidobenzenaldehyde hydrochloride* crystallises in slender needles which decompose above  $250^{\circ}$ , and when treated with sodium acetate yield the *monacetate*, and not the free base; the *triacetyl* derivative crystallises in needles melting at  $178$ – $179^{\circ}$ . All three amido-groups readily undergo the diazo-reaction, and the base, therefore, yields a colouring matter containing three naphthol groups. The reduction of nitrobenzenylnitrophenyleneamidine does not yield the corresponding base, but a compound,  $C_{13}H_{12}N_4O + H_2O$ , which is probably an oxydiamidophenylbenzimidazole, the *acetyl* derivative being a crystalline powder and melting at  $150^{\circ}$ . An attempt was made to ascertain the exact constitution of nitrobenzaldehyde by synthesis from  $\alpha$ -dinitrodibenzylaniline; oxidation with chromic acid, however, does not remove a benzyl group from this compound, as might be expected, but yields  $\alpha$ -dinitraniline.

Comparative dyeing experiments were carried out with the various colouring matters obtained from the bases described, and it was found that: 1. The fastness of the colouring matter increases with the number of azo-groups present. 2. An azo-group in the benzimidazole ring is more efficacious in producing a fast colour than one in the benzyl or phenyl group. 3. Compounds containing the azo-group in the benzimidazole ring give brown or bluish-brown shades; those containing it in the other groups produce yellowish or reddish-brown shades.

A. H.

**Combination of Phenylhydrazine and Alkylid Iodides.** By P. GENVRESSE and PAUL BOURCET (*Compt. rend.*, 1899, 128, 564–566).—The violent reaction between phenylhydrazine and alkylid iodides can be moderated by means of solvents such as alcohol or ether.

Methylic iodide yields two compounds: the first,  $N_2H_2Me_2PhI$ , forms long, monoclinic prisms, which melt and decompose at  $122^\circ$ , dissolve in water, especially if hot, but are almost insoluble in alcohol, and insoluble in ether. It is practically not attacked by hot concentrated potassium hydroxide solution, but reacts with silver oxide; gives a blue precipitate with Fehling's solution, but does not reduce it, a white precipitate with mercuric chloride, a pale yellow precipitate with lead acetate, a yellow precipitate with silver nitrate insoluble in sodium thiosulphate, a red precipitate with cupric sulphate, and a rust-coloured precipitate with ferric chloride. The second compound,  $2N_2H_3Ph.MeI$ , forms slender, white needles soluble in alcohol and very soluble in water, but insoluble in ether; it melts and decomposes at  $125^\circ$ . It reduces Fehling's solution, silver nitrate, and gold and platinum chlorides. Both compounds are somewhat unstable, but the second is much more liable to decompose than the first.

Ethylic iodide yields analogous compounds, which, however, are more readily purified and are much more stable; the compound insoluble in alcohol melts and decomposes at  $116^\circ$ , and the other melts to a yellow liquid at  $27^\circ$ .

C. H. B.

**Oxidation of Benzaldehydephenylhydrazone and Salicylaldehydephenylhydrazone by Air.** By HEINRICH BILTZ (*Annalen*, 1899, 305, 165—187. Compare Abstr., 1894, i, 584).—The compound described as a polymeride of salicylaldehydephenylhydrazone (*loc. cit.*) is not formed under conditions which preclude the possibility of oxidation; it may be obtained from a more labile isomeride arising from salicylaldehydephenylhydrazone on oxidation, and probably consists of salicilosazone,  $C_2(C_6H_4.OH)_2(N_2HPh)_2$ , because benzaldehydephenylhydrazone yields  $\alpha$ -benzilozazone when oxidised by air.

The transformation of benzaldehydephenylhydrazone into  $\alpha$ -benzilozazone is effected by passing a current of air into a solution of the aldehyde derivative in alcoholic potash heated in a reflux apparatus; the osazone has the properties described by Ingle and Mann (*Trans.*, 1895, 67, 606). The *acetyl* derivative is very readily soluble in chloroform, carbon bisulphide, acetic anhydride, and ethylic acetate, but dissolves with difficulty in methylic and ethylic alcohols; it melts indefinitely at  $80$ — $90^\circ$ , not having been obtained crystalline. The *acetyl* derivative of  $\beta$ -benzilozazone crystallises from alcohol in thin leaflets, and melts at  $183$ — $185^\circ$ .

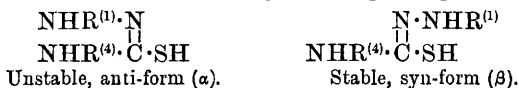
*Salicyl- $\alpha$ -osazone*,  $C_2(C_6H_4.OH)_2(N_2HPh)_2$ , prepared by oxidising salicylaldehydephenylhydrazone in alcoholic potash by air at the ordinary temperature, crystallises from ethylic acetate in aggregates of microscopic plates and melts at  $227$ — $228^\circ$ ; concentrated sulphuric acid develops an orange-red coloration, which rapidly darkens and ultimately becomes greenish. The *triacetyl* derivative cannot be recrystallised, and yields salicyl- $\beta$ -osazone on hydrolysis. The compound,  $C_{19}H_{13}N_2O_2$ , is a bye-product in the formation of salicyl- $\alpha$ -osazone; on adding alcohol to the solution in nitrobenzene, it crystallises in slender, deep red needles and melts at  $184^\circ$ . The solution in concentrated sulphuric acid is purple-violet.



*Salicyl-β-osazone* has been already described as a polymeric salicylaldehydephenylhydrazone (*loc. cit.*), and is obtained on treating the α-derivative with hot nitrobenzene, from which it crystallises in monoclinic leaflets melting at 281—282°. The *tetracetyl* derivative crystallises from ethylic acetate and melts at 244°. M. O. F.

**Nitrosalicylaldehydephenylhydrazones.** By HEINRICH BILTZ (*Annalen*, 1899, 305, 187—190).—5-Nitrosalicylaldehydephenylhydrazone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{N}_2\text{HPh}$  [ $\text{CH} : \text{OH} : \text{NO}_2 = 1 : 2 : 5$ ], crystallises from alcohol in rhombic, fluorescent leaflets, and melts at 194°; the *acetyl* derivative, which is not phenolic, melts at 165—166°, and yields a *silver* derivative. 3-Nitrosalicylaldehydephenylhydrazone, [ $\text{CH} : \text{OH} : \text{NO}_2 = 1 : 2 : 3$ ], crystallises from alcohol in dark red, rhombic plates, and melts at 138°; the *acetyl* derivative forms yellowish, pleochroic needles, and melts at 150°. M. O. F.

**Stereoisomeric Thiosemicarbazides. II.** By WILHELM MARCKWALD (*Ber.*, 1899, 32, 1081—1087. Compare *Abstr.*, 1893, i, 26).—As previously described, a thiosemicarbazide,  $\text{NHR}^{(1)} \cdot \text{N} : \text{C}(\text{SH}) \cdot \text{NHR}^{(4)}$ , is obtained by allowing a hydrazine,  $\text{NHR}^{(1)} \cdot \text{NH}_2$ , to remain with a thiocarbimide,  $\text{CS} : \text{NR}^{(4)}$ , in alcoholic solution at the ordinary temperature. Frequently it exists in two stereoisomeric forms, the unstable anti-form, which is first obtained, changing to the more stable syn-form when a little hydrochloric acid is added to its alcoholic solution, or when it is fused or subjected to prolonged heating.



These two forms are distinguished by treating a few centigrams with a benzene solution of carbonyl chloride, allowing the liquid to evaporate, warming the residue with ammonia, filtering and acidifying the filtrate with hydrochloric acid; if a precipitate forms, the original substance was an anti-compound, but if nothing more than an opalescence, a syn-compound. With carbonyl chloride, the syn-compound yields a thiobiazolone, which is neither acid nor basic in character, whilst the anti-form yields an imidobiazolone of acid character (in addition to some thiobiazolone, which probably results from a partial transformation of the anti- into the syn-form).



A great number of thiosemicarbazides has been prepared, and the following regularities have been observed with respect to the possibility of isomerism. (1.) Phenylhydrazine always unites with thiocarbimides, yielding unstable thiosemicarbazides of the anti-form, which are transformed into the stable syn-form when boiled with hydrogen chloride in alcoholic solution. (In this connection, it is noteworthy that 1-naphthylthiocarbimide forms no anti-thiosemicarbazides; 2-naphthylthiocarbimide, only very unstable ones, and none at all with phenylhydrazine itself). (2.) When the para-position in phenylhydrazine is

occupied, the resulting hydrazines behave like the parent substance. (3.) When the ortho- or meta-position is occupied, only stable thiosemicarbazides of the syn-form exist. (As might be anticipated from this, 1- and 2-naphthylhydrazines yield only syn-thiosemicarbazides; in the case of 1-naphthylhydrazine and phenylthiocarbimide, an isomeride melting at 135° is, indeed, obtained, but it, like the other compound, yields the thiobiazolone when treated with carbonyl chloride). (4.) The capacity for forming stereoisomeric thiosemicarbazides is entirely independent of the nature of the thiocarbimide, whether aliphatic or aromatic, and, in the latter case, whether substituted in the ortho-, meta-, or para-position. (5.) The unstable anti-isomerides always melt at lower temperatures than the stable stereoisomerides. (6.) Secondary hydrazines are incapable of yielding stereoisomeric forms.

The compounds obtained are enumerated, with their melting points, in the following table; a few of them have been described already, but most are new. The carbonyl chloride test was performed with all the thiosemicarbazides, but the melting point of the derivative obtained is only quoted when the latter was analysed.

$R^{(1)}$ .	$R^{(4)}$ .	Thiosemicarbazide.		Imido-biazolone.	Thio-biazolone.
		Anti.	Syn.		
Phenyl	Methyl	90—91°	163—164°	208°	240°
"	Phenyl	139	176	219—221	188
"	2-Tolyl	134	164	—	—
"	4- "	150	176	—	—
"	2 : 4-Xylyl	145	159	262	126
"	3-Chlorophenyl	120	168	—	—
"	4- "	133	165	—	—
4-Tolyl	Methyl	119	169—170	—	—
"	Phenyl	123	175	—	—
"	2-Tolyl	130—131	162—163	—	—
"	4- "	124—125	154	—	—
"	2 : 4-Xylyl	152	170	—	—
"	4-Chlorophenyl	145	146.5	275	229—230
4-Chlorophenyl	Ethyl	137—138	175	—	—
"	Phenyl	150	176—177	204—205	217
"	4-Chlorophenyl	142	160	249	155
4-Bromophenyl	Methyl	133	199	—	—
"	Ethyl	145—146	189—190	190	244
"	Phenyl	160	200	255	216
4-Nitrophenyl	Methyl	206	233	—	—
"	Phenyl	198—200	220	—	—
Phenyl	1-Naphthyl	—	183	—	160
4-Tolyl	"	—	184	—	—
2-Tolyl	"	—	176	—	—
4-Bromophenyl	"	—	185	—	—
Phenyl	2-Naphthyl	—	191	—	—
4-Tolyl	"	125	184	275	210
4-Bromophenyl	"	183	202	278	254

$R^{(1)}$ .	$R^{(2)}$ .	Semicarbazide (Syn).	Thiobiazolone.
2-Tolyl	Methyl	158—159°	—
"	Ethyl	130—131	—
"	Phenyl	146—147	197
"	2-Tolyl	148—149	—
"	4-Tolyl	141—142	—
2-Chlorophenyl	Methyl	147	—
"	Phenyl	156	171
2-Nitrophenyl	Methyl	201—202	—
"	Ethyl	167—168	—
"	Phenyl	185—186	—
2-Anisyl	Methyl	153	—
"	Phenyl	150—151	—
3-Chlorophenyl	Methyl	171	—
"	Phenyl	138—139	185—186
"	3-Chlorophenyl	142	—
3-Bromophenyl	Methyl	127—128	—
"	Phenyl	113	—
3-Nitrophenyl	Methyl	176—177	—
"	Phenyl	164	223
2:4-Xylyl	Methyl	179—180	—
"	Phenyl	149	158
2:4:5 Tribromophenyl	Methyl	206	—
"	Phenyl	203	—
"	4-Tolyl	201	—
1-Naphthyl	Methyl	195	—
"	Ethyl	149	—
"	Phenyl	(135) 220	224
"	4-Tolyl	169	—
"	1-Naphthyl	192	—
"	2- "	179	233
2-Naphthyl	Methyl	209	153
"	Ethyl	169	—
"	Phenyl	202	199
"	2-Tolyl	192	—
"	4- "	195	—
"	1-Naphthyl	207	—
"	2- "	187	—

*Methyl-* and *ethyl-benzyl-oxythiocarbamides*,  $\text{NHR} \cdot \text{CS} \cdot \text{NH} \cdot \text{O} \cdot \text{CH}_2\text{Ph}$ , were prepared by mixing alcoholic solutions of methyl and ethyl thiocarbimides with  $\alpha$ -benzylhydroxylamine; they melt at  $87^\circ$  and  $67^\circ$  respectively.  
C. F. B.

**Azonium Chromogens. III. Ethylnaphthaphenazonium and its Derivatives.** By W. G. SCHAPOSCHNIKOFF (*Chem. Centr.*, 1898, ii, 919—920; from *J. Russ. Chem. Soc.*, 30, 546—553. Compare this vol., i, 431).—*Amidoethylnaphthaphenazonium*, prepared by condensing dichloroquinonedi-imine with  $\beta$ -naphthylethylamine in alcoholic solution, separates in silky, golden needles, is easily soluble in water and alcohol, forms almost insoluble double salts with the chlorides of zinc, mercury, gold, and platinum, and, with potassium hydroxide, yields the free base as a violet, crystalline precipitate.

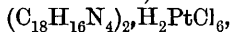
*Acetoethylisorosinduline*,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{---} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{EtCl} \end{smallmatrix} > C_6H_5 \cdot NHAc$ , prepared by the

action of acetic anhydride on the preceding compound, crystallises in lustrous, green prisms. *Ethyl-naphthaphenazonium* is obtained by diazotising amidoethylnaphthaphenazonium sulphate, or its acetyl derivative, dissolved in concentrated sulphuric acid, and then isolating it as the ferric chloride compound,  $C_{18}H_{16}N_2Cl \cdot FeCl_3$ , which melts at  $205^\circ$ , is decomposed by alkali carbonates, forming ferric oxide and ethylnaphthaphenazonium carbonate, and gives a yellow, crystalline precipitate with hydrochloric acid. The base itself is easily soluble in water, slightly in alcohol and acetic acid, and forms a *platinochloride*,  $(C_{18}H_{14}N_2)_2 \cdot H_2PtCl_6$ , as an orange, crystalline powder insoluble in cold water. *Ethylrosinduline*, prepared by the action of ammonia in alcoholic solution on ethylnaphthaphenazonium, forms a *nitrate* which separates in orange crystals, is soluble in water, and forms a fluorescent solution in alcohol. The base is precipitated in golden scales by alkalis or ammonia. *Dimethylethylrosinduline*, prepared by treating ethylnaphthaphenazonium with dimethylamine, forms salts which, on boiling in aqueous solution with acids or mineral salts, lose the

dimethylamine group and form *ethylrosindone*,  $O \begin{smallmatrix} \text{C}_{10}H_5 \cdot \text{N} \\ \text{---} \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{---} \\ \text{Et} \end{smallmatrix} > C_6H_4$ .

This compound, obtained also by boiling ethylnaphthaphenazonium or its salts with sodium hydroxide, is a feeble base, crystallises in lustrous, yellow scales, melts at  $180^\circ$ , and is soluble in alcohol and benzene.

*Dimethylethylisorosinduline*, in which the dimethylamido-group is contained in the benzene nucleus, is prepared by condensing ethyl- $\beta$ -naphthylamine with nitrosodimethylaniline hydrochloride; it is a violet pigment, and the *platinochloride*,  $(C_{20}H_{19}N_3)_2 \cdot H_2PtCl_6$ , is a dark green, crystalline powder. *Acetoethylnaphthaphenosafranine*, containing the  $NH_2$ -group in the nitrogen ring, the  $NHAc$ -group in the benzene ring, and both in the para-position with regard to the azine nitrogen, is prepared by the action of alcoholic ammonia on acetoethylisorosinduline in presence of air; it crystallises in green leaflets, and when dissolved in a 50 per cent. solution of sulphuric acid and boiled, yields *ethylnaphthaphenosafranine*, which crystallises from alcohol in small prisms with a metallic lustre, and is easily soluble in water and alcohol. The base is soluble in ether, and the *platinochloride*,



is a dark red, crystalline powder insoluble in water.

All these compounds are dyes. The replacement of the aromatic radicle of the quinevalent azine nitrogen by a fatty group has no greater effect on the properties of the compound than that of the acid group in the various salts of the same compound, but the compounds in which the substituted group is in the benzene ring are very different in colour and properties to those in which the group is in the naphthalene ring.

E. W. W.

**Constitution of the Azonium Compound from Benzil and Orthamidodiphenylamine.** By FRIEDRICH KEHRMANN and W. WOLFFSON (*Ber.*, 1899, 32, 1042—1045).—In a footnote to an earlier

communication (*Ber.*, 1891, 24, 1240), it was mentioned that from certain considerations it seemed probable that the azonium base obtained from benzil and orthamidodiphenylamine [phenylorthophenylenediamine] was in reality a tertiary alcohol, and that, on treating the azonium chloride with potassium hydroxide, a migration of the hydroxyl group had taken place from the azonium nitrogen to the neighbouring carbon atom of the ring. This view has now received support from the close similarity between the quinoxaline derivative formed by the condensation of benzoin and phenylorthophenylenediamine and the azonium base in question, the only difference being that, in one case, the red colour produced by alcoholic hydrochloric acid is permanent, whilst in the other it is merely temporary. If the formation of the azonium salt, however, is prevented, by converting the hydroxyl into an acetoxyl group by means of acetic anhydride, an *acetyl* compound which crystallises from benzene with benzene of crystallisation is produced; this, on treatment with alcoholic hydrochloric acid, gives a bluish-red coloration, permanent for months, and, on standing, deposits red crystals of the hydrochloride, a behaviour which is identical with that shown by the above mentioned benzoin condensation product.

J. F. T.

**Hydrolysis of Acid Amides.** By IRA REMSEN (*Amer. Chem. J.*, 1899, 21, 281—284).—In previous communications (*Abstr.*, 1878, 405; 1879, 52; 1880, 257), attention has been drawn to the protective action of an ortho-substituent on alkylic groups in the benzene nucleus during oxidation with chromic anhydride. In a preliminary note (*Abstr.*, 1897, i, 412), the protective influence of ortho-groups during the hydrolysis of substituted benzamides has also been noticed. The following abstract contains an account of experiments undertaken for the purpose of studying this protective influence more in detail.

J. J. S.

**Hydrolysis of Acid Amides.** By E. EMMET REID (*Amer. Chem. J.*, 1899, 21, 284—348. Compare preceding abstract, also Sudborough, Jackson, and Lloyd, *Trans.*, 1897, 71, 229).—The hydrolysis of substituted benzamides by dilute acids and alkalis has been studied by the aid of the equation,  $K = 2.3025 / (A - B)t \cdot \log. (A - x/B - x \cdot B/A)$ , where  $A$  and  $B$  represent the original concentrations of the acid (or alkali) and amide respectively, and  $A - x$  and  $B - x$ , their concentrations after  $t$  minutes.

A weighed quantity of the amide was heated with acid of the required strength on a water-bath, kept vigorously boiling, the flask being fitted with a reflux condenser and a syphon for removing part of the liquid after given intervals. The portion thus removed was run into cold water, the amount of ammonium salt estimated by boiling with magnesium hydroxide and collecting the ammonia in standard acid; the unaltered amide was then determined by boiling the residue with concentrated sodium hydroxide and again receiving the ammonia in standard acid.

Preliminary experiments made with the three nitrobenzamides indicate that when hydrochloric acid is employed, the ortho-compound is hydrolysed much more slowly than the meta- and para-derivatives, the constants for the latter changing but little with the concentration

of the acid. The ratio of the constants meta/para is approximately the same for both sulphuric and hydrochloric acids, the actual constants for sulphuric acid being those for hydrochloric  $\times 0.45$ . Alkalis gave large but decreasing constants and, when prepared by the addition of barium hydroxide to sodium or potassium sulphate solutions gave much lower results owing to the retarding action of the neutral salt present; pure barium hydroxide gave higher results owing to the absence of neutral salt.

A few experiments on the influence of temperature on the reaction indicate that between  $60^\circ$  and  $100^\circ$ , the values form a geometrical series.

The following values for the constant  $K$  have been obtained by the aid of  $0.5769\ N$  hydrochloric acid :

		$K$ .		
Benzamide .....		0.0209		
	Ortho.	Meta.	Para.	
Amidobenzamide .....	0.00178	0.01735	0.0198	}
			0.0177	
Chlorobenzamide .....	0.00321	—	0.0179	}
			†0.0204	
			†0.0196	}
Iodobenzamide .....	0.00106	—	—	
			0.0236	}
Nitrobenzamide .....	0.00054	0.0196	†0.0256	
Toluamide .....	0.00222	0.0193	0.0175	
Hydroxybenzamide .....	0.00437	—	—	
Methoxybenzamide .....	0.0116	—	—	
Ethoxybenzamide .....	0.0093	—	—	
		0.0184	0.0146	}
Bromobenzamide .....	—	†0.0210	†0.0186	
			†0.0173	

† These results were obtained when the concentration of the amide was half that employed in the other cases.

The results show that an ortho-substituent exerts a remarkable protective influence on the  $\cdot\text{CONH}_2$ -group. With similar groups, the influence varies roughly with the weight of the group, but otherwise appears to depend more on the nature of the group than on its mass; for example, the methyl group protects to a greater extent than does the heavier chlorine or methoxy-group. The nitro-group is remarkable for its great protective power (compare Kellas, Abstr., 1898, i, 86). Hydroxyl also protects to a greater extent than the methoxy- or ethoxy-group.

The results, in general, are in accord with those obtained by V. Meyer, Sudborough, Kellas, and others on the etherification of substituted benzoic acids, although the effect of the nature, rather than of the mass, of the substituent is brought more clearly into prominence.

J. J. S.

**Action of Oxidising Agents on some Amides.** By WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1899, 128, 503—505). Compare Abstr., 1898, 564, this vol., i, 243, 244, 420).—Phthalimide is decomposed at a somewhat high temperature by a mixture of potassium chromate solution and sulphuric acid, with liberation of carbonic

anhydride, but not of nitrogen. Potassium hydroxide and hydrogen peroxide decompose it very slowly, producing carbonic anhydride and ammonia.

Chromic mixture has very little action on succinamide, but partially decomposes glycocine and more readily attacks sarcosine. In no case is nitrogen liberated.

Formamide is violently attacked by potassium chromate solution and sulphuric acid, but nitrogen is not liberated; alkaline hydrogen peroxide converts it into ammonia and carbonic anhydride. Acetamide yields the same products, but is much less readily attacked. Benzamide is only partially decomposed by the chromate and sulphuric acid; nitrogen is not liberated, and a small quantity of benzonitrile is formed.

Formanilide is rapidly decomposed by chromic mixture, liberating carbonic anhydride and producing colouring matters. Acetanilide behaves in a similar way. C. H. B.

**2-Chlorophenylthiocarbimide.** By E. GROSCH (*Ber.*, 1899, 32, 1088—1089).—The compound described under this name by Hofmann (*Abstr.*, 1880, 387) must have been the para-isomeride, for orthochloraniline will not unite with carbon bisulphide, except to form chlorophenylic chlorophenylthiocarbamate. On the other hand, orthochloraniline (4 mols.) reacts with carbonyl chloride (1 mol.) in benzene solution, the product being diorthochlorophenylthiocarbamide, which melts at 141°. If only 3 mols. of orthochloraniline are taken, the product is *orthochlorophenyl thiocarbimide*,  $C_6H_4Cl \cdot N : CS$ ; this boils at 248° and does not solidify in the cold; with aniline, it yields an orthochlorodiphenylthiocarbamide identical with that obtained from phenylthiocarbimide and orthochloraniline. C. F. B.

**Synthesis of Aromatic Carboxylic Acids.** By LUDWIG GATTERMANN (*Ber.*, 1899, 32, 1116—1121).—The method formerly described by the author for preparing acid amides from aromatic hydrocarbons or phenol ethers (*Abstr.*, 1890, 974) is best carried out as follows: dry hydrogen chloride is passed over strongly heated cyanuric acid contained in a hard glass tube, and the chloroformamide thus formed led into a reflux apparatus containing the hydrocarbon or phenol ether, carbon bisulphide, and finely powdered aluminium chloride, the temperature being maintained at 30—40°. On cooling, two layers form, the lower of which is separated and poured into ice cold water, when nearly the theoretical yield of the required acid amide is obtained. To hydrolyse this to the corresponding carboxylic acid, a modification of Bouveault's method (*Abstr.*, 1893, ii, 541) is employed, which consists of adding sodium nitrite to a boiling solution of the amide in dilute sulphuric acid. By employing these methods, the author has prepared the following compounds.

[With PRENTICE].—*Isodurene-6-carboxylic acid*,  $C_6HMe_4 \cdot COOH$ , separates from light petroleum in colourless prisms and melts at 164—165°, whilst the *amide*,  $C_{11}H_{16}NO$ , crystallises from water in needles and melts at 141—142°; in accordance with Victor Meyer's law, the acid does not yield an ethereal salt when boiled for 3 hours with 3 per cent. alcoholic hydrogen chloride.

When durene is treated by the new method, it gives rise to a mixture of the amides of durenecarboxylic, isodurenecarboxylic, and prehnitolcarboxylic acids; durenecarboxylic acid, however, can readily be obtained pure by treating the hydrocarbon with chloroformamide in presence of aluminium chloride at  $0^\circ$  (compare Abstr., 1887, 569, and 1888, 574), and hydrolysing the resulting amide with nitrous acid; it melts at  $177^\circ$ , not at  $112^\circ$  as formerly stated.

[With KJELLBOM.]—*Paradiphenylbenzamide*,  $C_6H_4Ph \cdot CO \cdot NH_2$ , crystallises from acetic acid in colourless needles and melts at  $222\text{--}223^\circ$ , whilst *parapropoxybenzamide*,  $C_{10}H_{13}NO_2$ , separates from dilute alcohol in colourless needles and melts at  $154^\circ$ .

[With EUGEN OBERLÄNDER.]—The *amide*,  $OMe \cdot C_6H_2MePr_3 \cdot CO \cdot NH_2$ , prepared from carvacrylic methylic ether, crystallises from dilute alcohol in colourless needles, melts at  $163\text{--}164^\circ$ , and on hydrolysis yields the corresponding *acid*,  $C_{12}H_{16}O_3$ , which forms colourless, lustrous needles and melts at  $154\text{--}155^\circ$ ; the *amide*,  $C_{13}H_{19}NO_2$ , prepared from carvacrylic ethylic ether, has similar properties and melts at  $133\text{--}134^\circ$ , whilst the *acid*,  $C_{13}H_{18}O_3$ , prepared from it crystallises from water in colourless needles and melts at  $133^\circ$ .

[With J. A. RÖLOFSEN.]—*Orthochloroparanisamide*,  $OMe \cdot C_6H_3Cl \cdot CO \cdot NH_2$ , prepared from orthochloranisoil, crystallises from water in colourless needles and melts at  $193^\circ$ , whilst *orthobromoparanisamide* has similar properties and melts at  $185^\circ$ .

From the examples given, it appears that, in the treatment of phenolic ethers by the above method, the  $\cdot CO \cdot NH_2$ -radicle always takes up a para-position with regard to the alkyloxy-radicle. W. A. D.

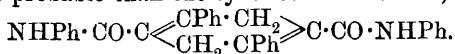
**Action of Aniline and Phenylcarbimide on Ketonic Acids of the  $C_nH_{2n-10}O_3$  Series.** By TIMOTHÉE KLOBB (*Bull. Soc. Chim.*, 1898, [iii], 19, 389—399).—Haller has shown that phenylcarbimide reacts with carboxylic acids to form acid anhydrides or anilides, according to the temperature employed. The author has applied this reaction to certain  $\gamma$ -ketonic acids, and obtained some new compounds derived from the anilides by the elimination of water.

When  $\beta$ -benzoylpropionic acid is heated with phenylcarbimide at a temperature not exceeding  $90\text{--}100^\circ$ , a yellow, viscous, odorous substance is obtained which is in all probability the true *anhydride* of the acid, since it is wholly converted into the latter by prolonged boiling with water, and is quite different from the phenylcrotonolactone which Fittig (Abstr., 1898, i, 196) obtained by the action of acetic anhydride on  $\beta$ -benzoylpropionic acid. If, however, the heating is continued until a temperature of  $200^\circ$  is reached, the principal product of the reaction is a *substance* crystallising in slender, yellow needles melting at  $195^\circ$ , whilst a variable quantity of the anilide is also formed. If 1 mol. of  $\beta$ -benzoylpropionic acid is heated with 2 mols. of phenylcarbimide, the yellow substance is exclusively formed, whilst if aniline is employed instead of phenylcarbimide, the anilide is the principal product.  $\beta$ -Benzoylpropionanilide, which has previously been obtained by Biedermann, crystallises from boiling benzene in thin leaflets, and from alcohol in large plates which melt



at  $145^{\circ}$  and are very soluble in alcohol, acetic acid, and chloroform, insoluble in light petroleum; when heated with fuming hydrochloric acid at  $100^{\circ}$ , it is quantitatively converted into aniline and  $\beta$ -benzoylpropionic acid. The yellow substance melting at  $195^{\circ}$  has the molecular formula  $C_{32}H_{26}N_2O_2$ , and is derived from 2 mols. of the anilide of  $\beta$ -benzoylpropionic acid by elimination of 2 mols. of water; the

constitution  $NHPh \cdot CO \cdot CH_2 \cdot CH_2 \cdot CPh : C \begin{smallmatrix} \swarrow CO \cdot NPh \\ \searrow CH : CPh \end{smallmatrix}$  is suggested as being more probable than the symmetrical formula,



The latter is inconsistent with the instability of the compound, as shown by its resolution into aniline and  $\beta$ -benzoylpropionic acid by the action of fuming hydrochloric acid at  $150^{\circ}$ , whilst the former explains the fact that no analogous compound is obtained from  $\beta$ -benzoyl- $\alpha$ -methylpropionic acid, in which there is only 1 atom of hydrogen available in the  $\alpha$ -position. It is very soluble in cold benzene, soluble in boiling chloroform, ether, and acetone, scarcely soluble in cold alcohol; it dissolves in concentrated sulphuric acid, from which it is reprecipitated unchanged by addition of water. When dissolved in alcoholic potash, the solution absorbs oxygen from the air, becomes brown, and, after some days, evolves an odour of phenylcarbamine, and contains a white, crystalline substance melting at about  $245^{\circ}$ .

$\beta$ -Benzoyl- $\alpha$ -methylpropionic acid, when heated at  $100^{\circ}$  with phenylcarbimide, yields a pale green, viscous substance of agreeable aromatic odour, which is doubtless the *anhydride* of the acid, but if the heating be continued up to a temperature of  $200^{\circ}$ , the principal product of the

reaction is 1:5-diphenyl-3-methylpyrrolone,  $CHMe \begin{smallmatrix} \swarrow CO \cdot NPh \\ \searrow CH : CPh \end{smallmatrix}$ ; this crystallises in colourless, monoclinic prisms, melts at  $128-130^{\circ}$ , sublimes without decomposition, and is very soluble in alcohol, acetic acid, and benzene. It does not absorb oxygen in presence of alcoholic potash, is not acted on by acetic anhydride at  $150^{\circ}$ , and is resolved by heating with fuming hydrochloric acid at  $100^{\circ}$  into aniline and  $\beta$ -benzoyl- $\alpha$ -methylpropionic acid. The *anilide* of the latter, which is obtained by the direct action of aniline on the acid, crystallises from boiling benzene in white needles melting at  $188-190^{\circ}$ , and subliming without decomposition. N. L.

**Propiophenoneorthocarboxylic Acid and Benzyl Methyl Ketone-orthocarboxylic Acid.** By JACOB GOTTLIEB (*Ber.*, 1899, 32, 958-967. Compare *Abstr.*, 1878, 735).—Ethylidenephthalide is most readily obtained by heating together perfectly dry sodium propionate, phthalic anhydride, and propionic anhydride for 1.5-2 hours at  $160-170^{\circ}$ ; the mixture is then warmed with water, and finally extracted with dilute acid, when the phthalide is left as a yellowish-red, crystalline mass, the yield being 88 per cent. of the propionic anhydride employed. As the phthalide, when kept for some time, becomes resinous, it is advisable to convert it at once into ortho-

propiophenonecarboxylic acid by warming with sodium hydroxide, and then precipitating with hydrochloric acid.

When warmed with phenylhydrazine, propiophenonecarboxylic acid yields 3-phenyl-1-ethylphthalazone,  $C_6H_4 \begin{smallmatrix} \text{C} \text{Et} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{N} \text{Ph} \end{smallmatrix}$ , which crystallises from alcohol in short, dark-yellow prisms melting at  $102^\circ$  and readily soluble in organic solvents.

Glycocine converts the acid into ethylidenephthalimidylacetic acid,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{CHMe}) \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{COOH}$  (compare Abstr., 1897, i, 59), which crystallises from acetic acid or dilute alcohol in prisms melting at  $205\text{--}207^\circ$ ; its *silver* salt,  $C_{12}H_{10}NO_3Ag$ , forms a white, crystalline precipitate.

Ethylphthalide,  $C_6H_4 \begin{smallmatrix} \text{CH} \text{Et} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{O}$ , obtained when the orthocarboxylic acid is reduced in alkaline solution with sodium amalgam, solidifies to a yellow, crystalline mass melting at  $12^\circ$  and distilling at  $291^\circ$  under 760 mm. pressure. The hydroxy-acid corresponding with this lactone has not been obtained in a pure form. Ethylnitrophthalide,  $C_{10}H_9N_4O$ , crystallises from alcohol in long, yellowish prisms melting and decomposing at  $63\text{--}64^\circ$ ; the nitro-group is probably in the meta-position to the ethyl group.

Orthopropylbenzoic acid is readily obtained when ethylphthalide is boiled for 96 hours in a reflux apparatus with red phosphorus and hydriodic acid boiling at  $127^\circ$ . The *silver* salt,  $C_{10}H_{11}O_2Ag$ ; *copper* salt,  $(C_{10}H_{11}O_2)_2Cu + 4H_2O$ ; *acid chloride*,  $C_6H_4Pr \cdot \text{COCl}$ , boiling at  $236^\circ$ ; *anilide*,  $C_6H_4Pr \cdot \text{CONHPh}$ , crystallising in prismatic plates and melting at  $108\text{--}109^\circ$ ; *ureide*,  $C_6H_4Pr \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , melting at  $171\text{--}172^\circ$ ; *amide*,  $C_6H_4Pr \cdot \text{CO} \cdot \text{NH}_2$ , melting at  $127\text{--}128^\circ$ ; *ethylic* salt boiling at  $244\text{--}247^\circ$  under 785 mm. pressure, and of sp. gr. 1.003 at  $15^\circ/15^\circ$ ; and *nitrile*, boiling at  $227\text{--}229^\circ$  under 758 mm. pressure, have all been prepared. The *thioamide*,  $C_6H_4Pr \cdot \text{CS} \cdot \text{NH}_2$ , obtained by the action of alcoholic ammonium sulphide on the nitrile at  $100^\circ$ , crystallises from its aqueous solution in long needles melting at  $53\text{--}54^\circ$ . Orthopropylaniline, obtained by the action of sodium hypobromite on orthopropylbenzamide, is a colourless liquid boiling at  $222\text{--}224^\circ$ .

Nitroorthopropylbenzoic acid,  $\text{NO}_2 \cdot C_6H_3Pr \cdot \text{COOH}$ , melts at  $116\text{--}118^\circ$ ; when reduced, it yields an *amido-acid* which crystallises from water in needles melting at  $157\text{--}158^\circ$ .

A better yield of methylisocoumarin (Abstr., 1893, i, 228) is obtained when  $\psi$ -diacetylorthobenzylic cyanide is boiled with aqueous phosphoric acid instead of with acetic and hydrochloric acids; when boiled with potassium hydroxide solution, it is converted into *benzyl methyl ketone-orthocarboxylic acid*,  $\text{COMe} \cdot \text{CH}_2 \cdot C_6H_4 \cdot \text{COOH}$ ; this forms broad, long needles, melts at  $118\text{--}119^\circ$ , and is soluble in the ordinary solvents. Its *silver* salt crystallises in slender, glistening needles, and its *copper* salt in dark green, glistening, anhydrous needles. Its *oxime* crystallises from 50 per cent. alcohol in slightly reddish plates melting at  $162^\circ$ , and when heated at  $162^\circ$  for 20 minutes is con-

verted into an *anhydride* which crystallises from acetone in needles melting at 171—173°. The *anhydride* of the *phenylhydrazone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CMe} : \text{N} \\ \text{CO} \text{-----} \end{smallmatrix} \text{NPh}$ , crystallises from alcohol in quadratic prisms melting at 198—199°, and is sparingly soluble in alcohol, ether, benzene, or acetic acid.

The orthocarboxylic acid readily reacts with glycocine at 160°, yielding a compound,  $\text{C}_{12}\text{H}_{11}\text{NO}_2$ , which melts and decomposes at 220°.

*Methylisocoumarin dibromide* crystallises from light petroleum in long prisms melting and decomposing at 64—66°. J. J. S.

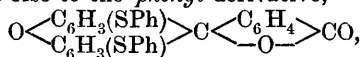
**Action of Isopropyllic Iodide on Phthalic Anhydride in Presence of Zinc Dust : Purification of Propylphthalide.** By PIETRO GUCCI (*Gazzetta*, 1898, 28, ii, 501—508).—On warming a mixture of zinc dust, isopropyllic iodide, and phthalic anhydride, a vigorous action takes place, large quantities of inflammable gas being evolved and an oil produced; the latter, when distilled under the ordinary pressure, yields propylene and phthalic anhydride, and, on hydrolysis, gives rise to isopropyllic alcohol, phthalic acid, isopropylphthalide, and the isobutyrylbenzoic acid obtained by Roser (Abstr., 1885, 267), by boiling isopropylidenephthalide with potash. From this, it is inferred that the products of the reaction are isopropyllic phthalate and isopropylphthalide,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CHPr}^i \\ \text{CO} \end{smallmatrix} \text{O}$ ;

the latter, after drying in ethereal solution by means of calcium chloride, and subsequently heating at 150° in a vacuum, boils at 225—229° under 160 mm. pressure.

When purified by this method, the normal propylphthalide already obtained by the author (Abstr., 1898, i, 665) boils at 230—234° under the same pressure. T. H. P.

**Thiofluorescein and Some Derivatives of the Phthaleins.** By LUDWIG GATTERMANN (*Ber.*, 1899, 32, 1127—1135).—[With ROBERT GANZERT].—Although, as stated by von Baeyer, fluorescein chloride is not converted into fluorescein by heating with alcoholic potash, it readily gives rise to thiofluorescein when heated with concentrated alcoholic potassium hydrosulphide for half an hour on the water-bath; thus obtained, thiofluorescein is a grey, amorphous powder, which is nearly insoluble in the ordinary solvents, does not melt below 300°, and dissolves in aqueous alkalis and ammonia with a more intensely blue coloration than that given by fluorescein under similar conditions. The colour, however, disappears when the alkaline solution is exposed for a long period to the air, owing to oxidation occurring, and is rapidly removed by warming with zinc dust; the colourless solution obtained in the latter case, however, again becomes blue when exposed to the air.

[With G. DE RIDDER].—When fluorescein chloride, dissolved in alcohol, is heated for half an hour with thiophenol and potassium hydroxide, it gives rise to the *phenyl* derivative,



of thiofluorescein, which crystallises from glacial acetic acid in colourless needles and melts at 197—198°.

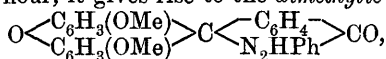
[WITH R. BERENDES].—The corresponding *orthotolyl* derivative,  $C_{34}H_{24}S_2O_3$ , prepared from orthothiocresol, crystallises from the same solvent in colourless prisms and melts at  $200-201^\circ$ . The isomeric *thiofluorescein ethers*,  $C_{36}H_{28}S_2O_5$ , prepared from orthethoxythiophenol and 4-methoxymetathiocresol, crystallise from glacial acetic acid in flesh-coloured needles and melt respectively at  $187^\circ$  and  $144-145^\circ$ .

[WITH F. BAMBERG].—The compound,  $C_{34}H_{24}S_2O_5$ , obtained from thioguaiacol, crystallises in rose-coloured needles and melts at  $212-213^\circ$ .

Dinitrophenolphthalein (Hall, Proc., 1893, 14; Errera and Berté, Abstr., 1896, i, 564) is conveniently prepared by carefully adding a mixture of concentrated nitric and sulphuric acids to a solution of phenolphthalein in glacial acetic acid cooled by ice, the temperature not being allowed to rise above  $20^\circ$ ; when heated with an excess of alcoholic potassium hydrosulphide, it is converted into *diamidophenolphthalein*,  $C_{20}H_{16}N_2O_4$ , which can also be obtained by reducing the dinitro-compound with stannous chloride, and is a greyish, crystalline powder. Alkaline solutions of the base have a deep blue colour, but soon become decolorised when exposed to the air.

[WITH ROBERT GANZERT].—When fluorescein is boiled for a short period with phenylhydrazine, it gives rise to the *phenylhydrazide*,  $O \begin{smallmatrix} \diagup C_6H_3(OH) \\ \diagdown C_6H_3(OH) \end{smallmatrix} > C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown N_2HPh \end{smallmatrix} > CO$ , which separates from ether and glacial acetic acid in colourless crystals, and dissolves in alkali giving a colourless, fluorescent solution; the *phenylhydrazide*,  $C_{26}H_{16}N_2Cl_2O_2$ , of fluorescein chloride, prepared by boiling the latter with phenylhydrazine, forms colourless needles, melts at  $265^\circ$ , and is insoluble in alkalis; *phenolphthalein phenylhydrazide*,  $C_{26}H_{20}N_2O_3$ , crystallises from glacial acetic acid in colourless needles, and dissolves in alkalis, giving a colourless solution.

[WITH CARL G. OEHMICHEN].—When fluorescein phenylhydrazide is heated with methylic iodide and an alcoholic solution of potassium hydroxide for an hour, it gives rise to the *dimethylic ether*,



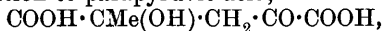
which crystallises from hot glacial acetic acid on adding water in colourless, silky needles and melts at  $227-228^\circ$ ; the corresponding *diethylic ether*,  $C_{30}H_{26}N_2O_4$ , forms slightly yellow-coloured, lustrous needles, and melts at  $247-248^\circ$ . The *dimethylic ether*,  $C_{28}H_{24}N_2O_3$ , of phenolphthaleinphenylhydrazide crystallises in yellow needles and melts at  $228^\circ$ , whilst the *diethyl* derivative,  $C_{30}H_{28}N_2O_3$ , forms colourless needles and melts at  $241-242^\circ$ .

When fluorescein is heated for a short time with concentrated hydrochloric acid at  $180^\circ$ , it gives rise to brownish-red plates of the *additive* compound,  $C_{20}H_{12}O_5 \cdot HCl$ , which is easily resolved by alkalis into its components, and is analogous to the additive compound obtained by von Baeyer from fluorescein and sulphuric acid (*Annalen*, 1862, 123, 27).

W. A. D.

**Synthesis of Uvitic Acid from Pyruvic Acid.** By LUDWIG WOLFF [and F. HEIP] (*Annalen*, 1899, 305, 125—153).—The change

by which pyruvic acid is converted into uvitic (symmetrical methyl-isophthalic) acid, first observed by Finck, has not yet been adequately explained. The author has isolated an intermediate product, methyl-dihydrotrimesic acid,  $C_{10}H_{10}O_6$ , and it is the elimination of hydrogen and carbonic anhydride from this substance which gives rise to uvitic acid, the two stages being represented by the equations I.  $4C_3H_4O_3 = C_{10}H_{10}O_6 + C_2H_2O_4 + 2H_2O$ . II.  $C_{10}H_{10}O_6 = C_9H_8O_4 + CO_2 + H_2$ . It is probable that 2 molecules of pyruvic acid first undergo condensation to parapyruvic acid,



(this vol., i, 483), 2 molecules of which then lose oxalic acid and water, yielding methyl-dihydrotrimesic acid.

*Methyl-dihydrotrimesic* (1 methyl- $\Delta^{2,4}$ -dihydrobenzene-1 : 3 : 5-tricarboxylic) acid,  $COOH \cdot CMe < \begin{smallmatrix} CH : C(COOH) \\ CH_2 \cdot C(COOH) \end{smallmatrix} > CH$ , prepared by heating pyruvic acid with aqueous soda during 2 hours in boiling water, crystallises from dilute alcohol in lustrous leaflets containing  $1H_2O$  which is lost at  $100^\circ$ ; it loses carbonic anhydride at  $195^\circ$ , and melts at  $245-250^\circ$ . The acid reduces Fehling's solution and potassium permanganate; it does not yield an additive compound with bromine, but is easily reduced by sodium amalgam, yielding methyltetrahydrotrimesic acid. Boiling baryta converts it slowly into uvitic acid. The *barium* salt contains  $8\frac{1}{2}H_2O$ , and is slowly decomposed by boiling water; the *methylic* salt, which crystallises from a mixture of ether and petroleum in small leaflets, sinters at  $72^\circ$  and melts at  $76^\circ$ .

When methyl-dihydrotrimesic acid is heated at  $200-240^\circ$  until carbonic anhydride ceases to be evolved, five hydrogenised isophthalic acids, in addition to uvitic acid, are produced.  $\Delta^{2,4}$ -Dihydrouvitic acid,  $CHMe < \begin{smallmatrix} CH : C(COOH) \\ CH_2 \cdot C(COOH) \end{smallmatrix} > CH$ , occurs in the boiling water extract of the fused methyl-dihydrotrimesic acid, and crystallises from hot water in small prisms melting at  $235-236^\circ$ ; the *barium* and *calcium* salts contain  $2\frac{1}{2}H_2O$  and  $3\frac{1}{2}H_2O$  respectively.  $\Delta^4$ -Tetrahydrouvitic acid,  $CHMe < \begin{smallmatrix} CH_2 \cdot CH(COOH) \\ CH_2 - C(COOH) \end{smallmatrix} > CH$ , dissolves more sparingly in water than the following three isomerides, and remains in association with dihydrouvitic acid when the fused methyl-dihydrotrimesic acid has been extracted with cold water; it crystallises from water in small plates melting at  $223-224^\circ$ , and is formed when dihydrouvitic acid is reduced with sodium amalgam.  $\alpha$ -Tetrahydrouvitic acid crystallises from hot water in large plates and melts at  $179-180^\circ$ .  $\beta$ -Tetrahydrouvitic acid melts at  $168-169^\circ$ ; it crystallises from water in long needles, and from dilute methylic alcohol in stout prisms.  $\gamma$ -Tetrahydrouvitic acid forms a colourless syrup, and is probably identical with uvitonic acid, obtained by Finck as a bye-product in the preparation of uvitic acid; the *calcium* salt contains  $1H_2O$ .

*Methyltetrahydrotrimesic* acid,  $COOH \cdot CMe < \begin{smallmatrix} CH_2 \cdot CH(COOH) \\ CH_2 - C(COOH) \end{smallmatrix} > CH$ , prepared by reducing methyl-dihydrotrimesic acid in alkaline solution with sodium amalgam, melts at  $220-222^\circ$ , slowly evolving gas; it crystallises from water in slender needles, and sometimes contains

$\text{H}_2\text{O}$ . Unlike methyldihydrotrimesic acid, it is indifferent towards boiling water, and yields only a small proportion of uvitic acid under the influence of concentrated sulphuric acid. The tetrahydro-acid reduces potassium permanganate, and is also oxidised by heated Fehling's solution; elimination of carbonic anhydride at  $230\text{--}240^\circ$  converts it into  $\alpha$ -tetrahydrouvitic acid.

When methyldihydrotrimesic acid is oxidised with cold potassium permanganate, uvitic acid is produced, the hot agent giving rise to trimesic acid; uvitic acid is also formed when the oxidation is carried out with ferric sulphate or nitric acid.

M. O. F.

**Action of Zinc and Ethylic Chloracetate on Ethylic Formate. Synthesis of Alkyllic Trimesates.** By SERGIUS N. REFORMATSKY (*Chem. Centr.*, 1898, ii, 472—473; from *J. Russ. Chem. Soc.*, 1898, 30, 280—292).—Ethylic trimesate, prepared by the action of ethylic chloracetate, or, better, bromacetate, on ethylic formate, separates from benzene in yellowish crystals, melts at  $133\cdot5\text{--}134\cdot5^\circ$ , is soluble in hot alcohol, ether, or acetic acid, and insoluble in water. Molecular weight determinations by Raoult's method gave unsatisfactory results. Trimesic acid forms delicate, white, hair-like crystals, melts above  $320^\circ$ , is easily soluble in alcohol and hot water, and slightly in cold water, 2·69 per cent. being dissolved by water at  $22\cdot5^\circ$  and 0·38 at  $16^\circ$ . The results obtained by titrating with barium hydroxide solution were too high. Methylic trimesate melts at  $142\cdot5^\circ$  (compare Piutti, *Abstr.*, 1887, 587). Several of the metallic salts of trimesic acid are described, amongst which the characteristic barium salt forms slender, hair-like crystals containing  $4\text{H}_2\text{O}$ , and the silver salt forms a flocculent, insoluble mass, which, on burning, swells like mercury thiocyanate. Ethylic trimesate is not formed by the action of zinc chloride on a mixture of ethylic acetate and ethylic formate.

E. W. W.

**Action of Sulphanilic Acid on Chloranil [Tetrachloroquinone] in Presence of Potash.** By H. IMBERT and J. PAGES (*Bull. Soc. Chim.*, 1898, [iii], 19, 575—576).—Sulphanilic acid has no action on tetrachloroquinone in presence of water alone, but if solid potash is gradually added to a boiling solution of potassium sulphanilate (2 mols.) and tetrachloroquinone (1 mol.) and the brown mass thus produced extracted with boiling water, a compound is obtained which has the formula  $\text{C}_6\text{Cl}_2\text{O}_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{K})_2$ . This substance crystallises in long, yellow needles which dissolve slightly in cold, much more readily in hot, water forming a greenish-brown solution which yields a brown precipitate with barium salts and also, on heating, with lead salts, but is not affected by salts of silver, mercury, or copper. Soda may be used instead of potash in the preparation of the new compound, and a similar reaction occurs with tetrabromoquinone.

N. L.

**Replacement of the Diazo-group by the Sulphinic Radicle.** By LUDWIG GATTERMANN (*Ber.*, 1899, 32, 1136—1159).—When a well-cooled aqueous solution of a diazo-sulphate containing an excess of sulphuric acid is saturated with sulphurous anhydride, and is subsequently surrounded by ice and gradually decomposed by adding copper-powder until no more nitrogen is evolved, the diazo-group is

replaced almost quantitatively by the sulphinic radicle  $\text{SO}_2\text{H}$ ; the sulphinic acid formed, according to its solubility in water, is isolated by extracting either the aqueous solution or the copper precipitate with ether, and is purified by dissolving in alkali, subsequently acidifying, again extracting with ether, and finally crystallising from water. Diazo-chlorides can also be employed in preparing sulphinic acids by this method, but in most cases the yield is smaller than with the corresponding sulphates. In some cases, notably with the naphthylamines, the method can profitably be modified by carefully adding the solution of the diazo-salt to the copper powder suspended in a saturated aqueous solution of sulphurous acid.

The decomposition probably takes place in three stages, as follows : (I)  $\text{R} \cdot \text{N}_2 \cdot \text{SO}_4\text{H} + \text{H}_2\text{SO}_3 = \text{R} \cdot \text{N}_2 \cdot \text{SO}_3\text{H} + \text{H}_2\text{SO}_4$ ; (II)  $\text{R} \cdot \text{N}_2 \cdot \text{SO}_3\text{H} - \text{O} = \text{R} \cdot \text{N}_2 \cdot \text{SO}_2\text{H}$ ; (III)  $\text{R} \cdot \text{N}_2 \cdot \text{SO}_2\text{H} = \text{N}_2 + \text{R} \cdot \text{SO}_2\text{H}$ . Quantitative determinations of the amount of copper passing into solution, as well as of the sulphuric acid formed, indicate that the reduction in equation II is effected by the copper powder, and not by the sulphurous acid employed.

The author cites a large number of examples of the application of the method, showing that, in nearly all cases, the yield is quantitative, and describes the following new compounds. Metaxylene-sulphinic acid,  $\text{C}_8\text{H}_9 \cdot \text{SO}_2\text{H}$ , crystallises from water in long, colourless needles and melts at  $77-78^\circ$ , not at  $50^\circ$  as stated by Jacobsen, whilst  $\psi$ -cumenesulphinic acid,  $\text{C}_9\text{H}_{11} \cdot \text{SO}_2\text{H}$ , melts at  $107-108^\circ$ , and not at  $98^\circ$  (Radloff, Abstr., 1878, 414), parachlorobenzenesulphinic acid at  $93-94^\circ$ , not at  $88-89^\circ$  (Otto and Brunner, *Annalen*, 143, 113), and parabromobenzenesulphinic acid at  $114-115^\circ$ , not at  $103^\circ$  (König, Abstr., 1892, 1091). *Orthanisolsulphinic acid*,  $\text{C}_7\text{H}_7\text{O} \cdot \text{SO}_2\text{H}$ , crystallises from water in stout, colourless needles, melts at  $98-99^\circ$ , and, when treated with nitrous acid (compare Königs, Abstr., 1878, 573), yields the compound  $(\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2)_2\text{N} \cdot \text{OH}$ , which separates from alcohol in colourless, lustrous needles, and melts at  $183-184^\circ$ ; *orthophenetoilsulphinic acid*,  $\text{C}_8\text{H}_9\text{O} \cdot \text{SO}_2\text{H}$ , crystallises from water in stout needles and melts at  $91-92^\circ$ ; *paranisolsulphinic acid* separates in long, lustrous needles and melts at  $97-98^\circ$ , whilst *paraphenetoilsulphinic acid* forms nacreous plates, melts at  $104^\circ$ , and yields, with nitrous acid, the compound  $\text{C}_{16}\text{H}_{19}\text{NS}_2\text{O}_7$ , which crystallises from alcohol in colourless needles and melts at  $161^\circ$ . *Methoxytoluenesulphinic acid* [ $\text{CH}_3 : \text{SO}_2\text{H} : \text{OMe} = 1 : 3 : 4$ ] forms long, colourless needles and melts at  $97^\circ$ ; *orthocarboxybenzenesulphinic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{H}$ , crystallises from glacial acetic acid or dilute alcohol in aggregates of needles, melts at  $125^\circ$ , and yields "saccharin" when heated with hydroxylamine for 3 hours at  $100^\circ$ ; *metacarboxybenzenesulphinic acid* crystallises from alcohol in stout prisms and melts at  $197-198^\circ$ . *Sodium naphthalene-1-sulphin-4-sulphonate*,  $\text{SO}_2\text{H} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{Na}$ , crystallises from water in small, colourless plates, whilst the acid,  $\text{C}_{10}\text{H}_6\text{S}_2\text{O}_5$ , forms lustrous, asbestos-like needles; *sodium naphthalene-1-sulphin-2-sulphonate*,  $\text{SO}_2\text{H} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_3\text{Na} + \text{H}_2\text{O}$ , separates from water in yellowish crystals, whilst *disodium naphthalene-2-sulphin-4 : 1'-disulphonate*,  $\text{SO}_2\text{H} \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})_2 + \text{H}_2\text{O}$ , crystallises from water, on adding alcohol, in colourless needles.

The following mercaptans have been prepared by reducing the corresponding sulphinic acids. *Metaxylylic mercaptan*,  $C_6H_3Me_2 \cdot SH$ , is a disagreeably smelling liquid which boils at  $207-208^\circ$ ; *paraxylylic mercaptan* boils at  $205-206^\circ$ , *orthomethoxythiophenol* at  $218-219^\circ$ , and its *methyl ether*,  $OMe \cdot C_6H_4 \cdot SMe$ , at  $237^\circ$ ; the *bisulphide*,  $S_2(C_6H_4 \cdot OMe)_2$ , prepared by adding finely powdered iodine to a solution of orthomethoxythiophenol in 10 per cent. caustic soda, crystallises from alcohol in lustrous, colourless needles and melts at  $119-120^\circ$ . *Orthethoxythiophenol*,  $C_8H_{10}SO$ , boils at  $226-227^\circ$ , and its *ethyl ether*,  $C_{10}H_{14}SO$ , at  $248-250^\circ$ , whilst the *bisulphide*,  $C_{16}H_{18}S_2O_2$ , crystallises from alcohol in stout needles and melts at  $89-90^\circ$ . *Paramethoxythiophenol* boils at  $227^\circ$ , its *methyl ether*,  $C_8H_{10}SO$ , at  $239-240^\circ$ , whilst the *bisulphide*,  $C_{14}H_{14}S_2O_2$ , melts at  $44-45^\circ$ ; *parethoxythiophenol* boils at  $238^\circ$ , its *ethyl ether* at  $259-260^\circ$ , whilst the *bisulphide* forms lustrous needles and melts at  $48-49^\circ$ . *Methoxythiocresol* [ $CH_3 : SH : OMe = 1 : 3 : 4$ ] boils at  $244-245^\circ$ ; its *methyl ether* crystallises from alcohol in long, colourless needles and melts at  $31.5^\circ$ , whilst the *bisulphide* forms lustrous plates and melts at  $64.5^\circ$ .

When orthocarboxybenzenesulphinic acid is reduced with zinc dust and hydrochloric acid, it forms a mixture of thiosalicyclic acid,  $SH \cdot C_6H_4 \cdot COOH$  (Gräbe and Aulich, German Patent 69073; List and Stein, Abstr., 1898, i, 584), and dithiosalicyclic acid,  $S_2(C_6H_4 \cdot COOH)_2$ ; the *sodium* salt,  $C_7H_5SNaO_2$ , of the former crystallises in large, yellowish plates, whilst the *methyl* salt,  $COOMe \cdot C_6H_4 \cdot SH$ , is a colourless oil which boils at  $252^\circ$ . Dithiosalicyclic acid, prepared by adding orthocarboxybenzenesulphinic acid dissolved in water to a hot solution of stannous chloride in concentrated hydrochloric acid, crystallises from alcohol in prisms and melts at  $289^\circ$ . Metacarboxybenzenesulphinic acid, when reduced with zinc dust and hydrochloric acid, yields the so-called "dithio-oxybenzoic acid" (dimetacarboxyphenylic bisulphide),  $S_2(C_6H_4 \cdot COOH)_2$ .

*Sodium 1-thionaphthol-4-sulphonate*,  $C_{10}H_7S_2O_3Na$ , prepared by reducing the corresponding sulphinic acid with tin and hydrochloric acid, crystallises from water in yellowish needles; when the reduction is carried out in concentrated solution, the *tin* salt,  $(SO_3Na \cdot C_{10}H_6 \cdot S)_2Sn$ , separates in yellow plates. The *tin* derivative,  $C_{20}H_{12}S_4O_6Na_2Sn$ , of sodium 1-thionaphthol-2-sulphonate is similarly obtained from naphthalene-1-sulphin-2-sulphonic acid, and crystallises from water in yellow needles. *Sodium 2-thionaphthol-4 : 1'-disulphonate*,  $C_{10}H_6S_2O_6Na_2$ , was also prepared.

The following sulphonic acids were obtained by oxidising the corresponding sulphinic derivatives with alkaline potassium permanganate. *Potassium orthanisolsulphonate*,  $C_7H_7SO_4K$ , crystallises from absolute alcohol; the corresponding amide,  $C_7H_9NSO_3$ , melts at  $169-170^\circ$ , whilst the *anilide*,  $C_{13}H_{13}NSO_3$ , crystallises from alcohol in lustrous plates and melts at  $161^\circ$ . *Potassium orthophenetoilsulphonate*,  $C_8H_9SO_4K$ , forms lustrous needles; the corresponding *chloride*, nacreous plates melting at  $65-66^\circ$ ; the *amide*, long needles melting at  $163^\circ$  (compare Lagai, Abstr., 1892, 1089); the *anilide*, large plates melting at  $158^\circ$ , and the *phenylhydrazide*, silky needles which melt at  $132-133^\circ$ . *Potassium paranisolsulphonate*,  $C_7H_7SO_4K$ , crystallises from alcohol



in sheaf-like aggregates of needles; the corresponding *amide* melts at  $116^\circ$ , and the *anilide* at  $110-111^\circ$ ; the properties of the corresponding phenetol derivatives are those given by Lagai (*loc. cit.*). *Potassium methoxytoluenesulphonate*,  $C_8H_9SO_4K$  [ $CH_3 : SO_3K : OCH_3 = 1 : 3 : 4$ ], forms lustrous plates, the *chloride* crystallises from light petroleum in flattened needles, and melts at  $67-67.5^\circ$ ; the *amide* separates from alcohol in silky needles and melts at  $138^\circ$ , whilst the *anilide* melts at  $163^\circ$ . 1:4-Naphthalenedisulphonic acid is more easily prepared by oxidising naphthalene-1-sulphin-4-sulphonic acid than by Armstrong and Wynne's method (Proc., 1893, 166); the *amide*,  $C_{10}H_{10}N_2S_2O_4$ , crystallises from dilute alcohol in needles and melts at  $273^\circ$ , whilst the *anilide*,  $C_{22}H_{18}N_2S_2O_4$ , forms leaflets and melts at  $179^\circ$ .

When sodium hydrogen 1:4-naphthalenedisulphonate is nitrated in sulphuric acid solution and the nitro-derivative reduced by stannous chloride, *sodium hydrogen amidonaphthalenedisulphonate*,  $SO_3H \cdot C_{10}H_5(NH_2) \cdot SO_3Na + 1\frac{1}{2}H_2O$  [ $SO_3H : SO_3Na : NH_2 = 1 : 4 : 1$ ], is obtained in brownish cubes, which are sparingly soluble in water; that the amido-group is in the  $\alpha$ -position is shown by the sodium salt yielding  $\alpha$ -naphthylamine when reduced by sodium amalgam. *Naphthalene-1:4:1'-trisulphonic chloride* crystallises in beautiful needles and melts at  $156-157^\circ$ ; *sodium 1':1-naphthasultone-4-sulphonate*,  $C_{10}H_5S_2O_6Na + \frac{1}{2}H_2O$ , obtained on diazotising the corresponding sodium hydrogen amidonaphthalenedisulphonate and boiling with water, crystallises in beautiful, efflorescent needles, and, on reduction, yields  $\alpha$ -naphthol. *Trisodium naphthalene-2:4:1'-trisulphonate*,  $C_{10}H_5S_3O_9Na_3$ , prepared from naphthalene-2-sulphin-4:1'-disulphonic acid, crystallises from alcohol in colourless needles, whilst the corresponding *chloride*,  $C_{10}H_5S_3Cl_3O_6$ , forms well-defined crystals and melts at  $146^\circ$ .

W. A. D.

**Etard's Reaction.** By MAX WEILER (*Ber.*, 1899, 32, 1050-1056).—Paraditolyl, diphenylmethane, paratolylphenylmethane, or dibenzyl (1 mol.) was dissolved in carbon bisulphide and treated with a solution of chromyl chloride (2 mols.) in the same solvent, added in successive small portions at the ordinary temperature (compare Etard, *Abstr.*, 1881, 581); the carbon bisulphide solution and the chromate precipitate were then worked up separately, the latter being decomposed with water. It was found that the chromyl chloride acted to some extent as a chlorinating, although mainly as an oxidising, agent.

Diphenylmethane yields benzophenone as sole product.

Paratolylphenylmethane yields phenyl paratolyl ketone together with some parabenzy benzaldehyde and chlorotolylphenylmethane,  $CH_2Ph \cdot C_6H_4 \cdot CH_2Cl$ .

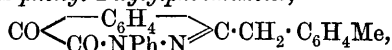
Paraditolyl yields 4'-tolyl-4-benzaldehyde,  $C_6H_4Me \cdot C_6H_4 \cdot CHO$ , melting at  $105-106^\circ$ , together with a *chloroditolyl*,  $C_6H_4Me \cdot C_6H_4 \cdot CH_2Cl$ , which melts at  $109^\circ$  after softening at  $105^\circ$ , and a little *dichloroditolyl*,  $CH_2Cl \cdot C_6H_4 \cdot C_6H_4 \cdot CH_2Cl$ , melting at  $136-138^\circ$ .

Dibenzyl yields benzaldehyde, some benzil and benzoin, deoxybenzoin, and benzophenone, together with  $\alpha$ -stilbene dichloride and stilbene hydrochloride.

C. F. B.

**2-Xylalphthalide.** By FRITZ BETHMANN (*Ber.*, 1899, 32, 1104—1113. Compare Heilmann, *Abstr.*, 1891, 200, and A. Ruhemann, *Abstr.*, 1892, 473, for 3- and 4-xylalphthalides).—*2-Xylalphthalide*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Me}$ , is obtained by heating phthalic anhydride (1 part) with 2-tolylacetic acid (1 part) and sodium acetate (0.02 part) for 10 hours at 240—250°, not more than 15—20 grams being used in one operation; it is yellow, and melts at 136.5°. When heated with aqueous caustic potash, it yields *α-2-methyldeoxybenzoin-2'-carboxylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ ; this melts at 131°, and forms a blue, insoluble copper salt, which melts at 179°, after softening at 160°. The *amide* of this acid is obtained when the phthalide is heated with alcoholic ammonia for 2 hours at 100°; it is yellowish-white, and melts at 155°; when boiled with acetic acid for 10 minutes, it yields *2-xylalphthalimidine*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Me}$ , which is yellow, and melts at 196—197°.

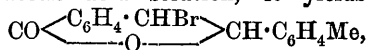
*α-2-Methyldeoxybenzoin-2'-carboxylic acid* yields the *oximidolactone* of *phenyl-2-xyllylketoxime-2'-carboxylic acid*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , melting at 138.5° when it is dissolved in aqueous soda, the solution boiled with hydroxylamine, and then acidified with hydrochloric acid. When it is boiled with phenylhydrazine and acetic acid in alcoholic solution, it yields *phenyl-2-xyllylphthalazone*,



which melts at 177°; when it is reduced in cooled alkaline solution with 2½ per cent. sodium amalgam, it yields the sodium salt of *α-2'-methyltoluylenehydrate-2-carboxylic* [*α-hydroxy-2'-methyl dibenzyl-2-carboxylic*] acid,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ ; when this is decomposed with hydrochloric acid and the precipitate crystallised from alcohol, monoclinic crystals [*a*:*b*:*c* = 1:1:0.7880; β = 113½°] of *2-xyllylphthalide*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , melting at 87°,

are obtained. If the alkaline solution is not decomposed with hydrochloric acid, but concentrated on the water-bath, a syrup separates, and this, when heated for 5 hours at 200° and treated with dilute hydrochloric acid, yields *2'-methylstilbene-2-carboxylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Me}$ , which melts at 169°; its green, insoluble copper salt melts and decomposes at about 150°.

*2-Methylstilbene-2-carboxylic acid*, when reduced with 2½ per cent. sodium amalgam in alkaline solution, yields *2'-methyl dibenzyl-2-carboxylic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , which melts at 123°. When treated with bromine in acetic acid solution, it yields *bromo-2-tolylidihydroisocoumarin*,



melting at 101—102°; if the product, instead of being precipitated with water, is boiled down and distilled under a pressure of 12 mm., the bromine is entirely removed; acetic acid distils over first, and then, at 220—240°, *2-tolylisocoumarin*,  $\text{CO} \langle \text{C}_6\text{H}_4 \cdot \text{CH} \rangle \text{C} \cdot \text{C}_6\text{H}_4\text{Me}$ ,

which forms yellow, rhombic crystals [ $a:b:c=0.7526:1:0.5499$ ] and melts at  $102.5^{\circ}$ .

2-Tolylisocoumarin, when treated with concentrated caustic potash solution, yields a syrup from which hydrochloric acid precipitates  $\beta$ -2'-methyldeoxybenzoin-2-carboxylic acid,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$ , melting at  $139^{\circ}$ . When this acid is reduced with sodium amalgam in alkaline solution, the product is  $\beta$ -hydroxy-2'-methyl dibenzyl-2-carboxylic acid,  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$ , which melts and decomposes at  $137^{\circ}$ . When the potassium salt of this acid is heated, 2'-methylstilbene-2-carboxylic acid (see above) is formed; but when the free acid is heated to  $150^{\circ}$ , the product is 2-tolyldihydroisocoumarin,  $\text{CO}\langle\text{C}_6\text{H}_4\cdot\text{CH}_2\rangle\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , which melts at  $117^{\circ}$ . When 2-tolylisocoumarin is heated with alcoholic ammonia for 12 hours at  $100^{\circ}$ , 2-tolylisocarbostyryl,  $\text{CO}\langle\text{C}_6\text{H}_4\cdot\text{CH}\rangle_{\text{NH}}\text{C}\cdot\text{C}_6\text{H}_4\text{Me}$ , melting at  $179^{\circ}$ , is formed, and when this is heated with phosphorus oxychloride for half an hour on the water-bath, the product is chloro-2-tolyisoquinoline,  $\text{CCl}\langle\text{C}_6\text{H}_4\cdot\text{CH}\rangle_{\text{N}}\text{C}\cdot\text{C}_6\text{H}_4\text{Me}$ , which melts at  $67^{\circ}$ , forms monoclinic crystals [ $a:b:c=1.3586:1:1.05065$ ;  $\beta=119^{\circ} 45'$ ], and yields 2-tolyisoquinoline when boiled for 3 hours with hydriodic acid (boiling at  $127^{\circ}$ ) and red phosphorus. The last base melts at  $78-79^{\circ}$ ; its hydrochloride, hydrobromide, yellow hydriodide, picrate, sulphate, and orange platinochloride (with  $2\text{H}_2\text{O}$ ) melt and decompose at about  $221^{\circ}$ ,  $235^{\circ}$ ,  $190^{\circ}$ ,  $150^{\circ}$ ,  $212^{\circ}$ , and  $210^{\circ}$  respectively. C. F. B.

Action of the Bis-diazochlorides of Benzdine, Orthotolidine, and Dianisidine on Ethylic and Methylic Malonates. By G. FAYREL (*Compt. rend.*, 1899, 128, 829—830. Compare this vol., i, 438).—The action of these malonates on tetrazodiphenyl chloride yields ethylic diphenyldihydrazonemalonate,  $\text{C}_{12}\text{H}_8[\text{NH}\cdot\text{N}:\text{C}(\text{COOEt})_2]_2$ , which forms yellow lamellæ melting at  $178-180^{\circ}$ , and the methylic salt which melts at  $217-220^{\circ}$ . Tetrazo-orthoditolyl chloride, under similar conditions, yields ethylic ditolyldihydrazonemalonate melting at  $188-190^{\circ}$ , and the methylic salt which melts at  $210-212^{\circ}$ , whilst the bis-diazochloride prepared from dianisidine yields ethylic ortho-dianisyldihydrazonemalonate which melts at  $190-192^{\circ}$ , and the methylic salt which melts at  $268-270^{\circ}$ . C. H. B.

Phenyldimethylcoumalin. By Ugo Bossi (*Gazzetta*, 1899, 29, i, 1—12).—Ciamician and Silber (*Abstr.*, 1894, i, 300) showed that, on treatment with alkalis, phenylcoumalin is resolved into acetophenone and formylacetic acid; this transformation they regard as taking place in several stages, the lactone giving first a hydroxy-acid, then a ketonic acid, which, by taking up a mol. of water, is converted into acetophenone and formylacetic acid. They were not able, however, to isolate the intermediate ketonic acid, namely,  $\gamma$ -benzoylcrotonic acid.

In the case of the phenyldimethylcoumalin prepared by Ciamician and Silber (*loc. cit.*), the author finds that, on interaction with the calculated quantity of cold alcoholic potash, it gives as sole product

*benzoyldimethylcrotonic acid*,  $\text{CPh} \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOH}$ . This acid separates in two forms; one, probably the fumaroid compound, crystallising from light petroleum in star-shaped groups of fine needles which melt at  $101^\circ$ , and are insoluble in water, slightly soluble in light petroleum, more so in aqueous alcohol, benzene, or ethylic acetate. The other, probably the maleoid form, is an oil having a characteristic odour, and is converted by concentrated hydrochloric acid into the fumaroid isomeride.

By the action of phenylhydrazine on benzoyldimethylcrotonic acid, no hydrazone is obtained, but 1 : 3-*diphenyl*-4 : 5-*dimethyl*-5-*pyrazoline*-acetic acid,  $\begin{array}{c} \text{CPh} \cdot \text{CHMe} \\ \parallel \quad \parallel \\ \text{N} \text{---} \text{NPh} \end{array} > \text{CMe} \cdot \text{CH}_2 \cdot \text{COOH}$ , which crystallises in shining, yellow scales, melts at  $169\text{--}170^\circ$ , and is slightly soluble in light petroleum, more so in benzene and ethylic acetate. It forms an unstable silver salt, but its potassium, sodium, barium, calcium, and strontium salts are stable and crystallise from water in lustrous yellow laminae.

Hydroxylamine resembles phenylhydrazine in its action on dimethylbenzoylcrotonic acid, giving 2-*phenyl*-3 : 4-*dimethyl*-4-*isoxazole*-acetic acid,  $\text{CPh} < \begin{array}{c} \text{CHMe} \\ \text{N} \text{---} \text{O} \end{array} > \text{CMe} \cdot \text{CH}_2 \cdot \text{COOH}$ , a yellow oil soluble in solutions of alkalis, alkali carbonates, and ammonia, and forming a stable silver salt.

On reduction with sodium amalgam, benzoyldimethylcrotonic acid gives a mixture of di- and tetra-hydrodimethylphenylcoumalins, and on treatment with ammonium acetate and acetic acid it yields 2-*phenyl*-3 : 4-*dimethyl*-6-*pyridone* ( $\alpha$ -phenyl- $\alpha'$ -lutidone), which crystallises from benzene in colourless, transparent rhombohedra melting at  $166^\circ$ .  
T. H. P.

**Reactions of Indones and Quinones with Derivatives of Malonic Acid.** By CARL LIEBERMANN (*Ber.*, 1899, 32, 916—925. Compare this vol., i, 373).—Dihalogen derivatives of indones and quinones, as a rule, react only with 1 mol. of a derivative of malonic acid, but with ethylic cyanacetate in some cases both the halogen atoms are replaced. Dichlorindone reacts only with 1 mol. of this substance, yielding *ethylic chlorindonecyanacetate*,  $\text{CO} < \begin{array}{c} \text{CCl} \\ \text{C}_6\text{H}_4 \end{array} > \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt}$ , which crystallises in colourless needles melting at  $118^\circ$ .

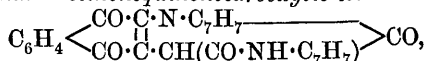
Dibromindone yields a mixture of *ethylic bromindonecyanacetate*,  $\text{C}_{14}\text{H}_{10}\text{BrNO}_3$ , melting at  $134\text{--}135^\circ$ , and *diethylic indonedicyanacetate*,  $\text{CO} \text{---} \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt}$ ,  $\begin{array}{c} \parallel \\ \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt}$ , which forms yellow crystals melting at  $142\text{--}143^\circ$ . 2 : 3-Dichloro- $\alpha$ -naphthaquinone behaves in a similar manner, yielding *ethylic chloro- $\alpha$ -naphthaquinonecyanacetate*,  $\text{C}_{15}\text{H}_{10}\text{ClNO}_4$ , melting at  $118^\circ$ , and *diethylic  $\alpha$ -naphthaquinonedicyanacetate*,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt} \\ \parallel \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{CN}) \cdot \text{COOEt} \end{array}$ , melting at  $203\text{--}204^\circ$ .

The halogen atom of the monohalogen product formed from a

dihalogen quinone and 1 mol. of a derivative of malonic acid can be readily replaced by substituted amido-groups. Ethylic bromo- $\alpha$ -naphthaquinonemalonate readily reacts with ethylamine, forming *ethylic ethyl-naphthindolinonequinonecarboxylate*, 
$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{N} \text{Et} \\ \parallel \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{COOEt}) \end{array} > \text{CO},$$

which is probably formed from the direct product of the action of ethylamine by the loss of the elements of alcohol. This substance crystallises in silky, yellow needles, which melt and decompose at  $195^\circ$ , and forms a blue solution in dilute alkalis and alkali carbonates. It is accompanied by a second compound containing bromine and nitrogen, which crystallises in red prisms and melts at  $131^\circ$ .

*Paratolyl-naphthindolinonequinonecarboxylic toluidide*,



is prepared by boiling ethylic bromonaphthaquinonemalonate with alcoholic toluidine, and crystallises in red needles melting at  $285^\circ$ . When the boiling is only continued for a short time, on the other hand, the product consists of the *paratoluidide* of *diethylic  $\alpha$ -naphthaquinone-malonate*, 
$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{C}_7\text{H}_7 \\ \parallel \\ \text{CO} \cdot \text{C} \cdot \text{CH}(\text{COOEt})_2 \end{array},$$
 which crystallises in red needles melting at  $122$ – $124^\circ$ .

Bischlorindonephloroglucinol is converted by acetic anhydride and sodium acetate into a *triacetyl* derivative,  $\text{C}_6\text{H}(\text{OAc})_3 \left( \text{C} \begin{array}{c} \text{CO} \\ \parallel \\ \text{CCl} \end{array} > \text{C}_6\text{H}_4 \right)_2$ , melting at  $203^\circ$ . This shows that, in its reaction with dichlorindone, phloroglucinol has behaved as a hydroxyl derivative, and not as a ketone.

*Chlorindoneresorcinol ether*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \parallel \\ \text{CCl} \end{array} > \text{C} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , obtained by the action of resorcinol on dichlorindone in the presence of sodium ethoxide in the cold, crystallises in yellow needles melting at  $163$ – $164^\circ$ , and forms an *acetyl* derivative melting at  $97$ – $98^\circ$ . In boiling alcoholic solution, however, resorcinol yields *anhydroindoneresorcinol ether*, 
$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} - \text{C} \cdot \text{O} \\ \parallel \\ \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{OH} \end{array}$$
 which crystallises in red needles, decomposes when heated, and forms a blue solution in cold aqueous sodium carbonate; its *acetyl* derivative forms light-red, matted needles melting at  $191$ – $192^\circ$ .

*Anhydro- $\alpha$ -naphthaquinoneresorcinol*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{C} \cdot \text{C}_6\text{H}_3 \cdot \text{OH} \\ \parallel \\ \text{CO} \cdot \text{C} \cdot \text{O} \end{array}$ , crystallises in reddish needles melting above  $300^\circ$ , and yields an *acetyl* derivative melting at  $289^\circ$ .

Ethylic glutaconate reacts in a similar manner to ethylic malonate with indones and quinones, but the colour reactions of the products are somewhat different. A. H.

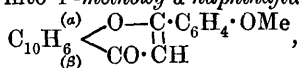
**3:2'-Dihydroxyflavone.** By STANISLAUS VON KOSTANECKI and R. VON SALIS (*Ber.*, 1899, 32, 1030–1034).—By combining ethylsalicylic aldehyde with the monethylic ether of resacetophenone, under the same conditions as were observed in the case of monethylic

ether of benzylideneresacetophenone, the *ethylic ether* of 2-ethoxybenzylideneresacetophenone,  $\text{OEt} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$  [= 4:2:2'], is formed; it crystallises from alcohol in reddish-yellow prisms melting at 125°. The *acetyl* derivative crystallises from alcohol in light yellow plates melting at 78—90°, and on treatment with bromine in carbon bisulphide solution takes up 2 atoms of bromine without evolution of hydrogen bromide, forming a thick syrup, which probably consists of the *dibromide*, since on treatment with alcoholic potassium hydroxide it yields 3:2'-diethoxyflavone,  $\text{OEt} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt} \\ \diagdown \end{smallmatrix} \text{CO} \cdot \text{CH}$  [OEt = 3:2']; this crystallises from

alcohol in prisms melting at 125°, and is coloured yellow by concentrated sulphuric acid, the solution gradually losing its colour and assuming a bright blue fluorescence.

On treatment with sodium ethoxide, 3:2'-diethoxyflavone is entirely resolved into the monethylic ether of resacetophenone and salicylic acid, and on treatment with hydriodic acid is converted into 3:2'-dihydroxyflavone, a substance which crystallises in microscopic needles melting at 320°; with sulphuric acid, it behaves in the same way as the diethylic ether, and dissolves in sodium hydroxide solution with a yellow coloration. 3:2'-Diacetoxyflavone crystallises from dilute alcohol in white crystals melting at 105°. J. F. T.

**4'-Hydroxy- $\alpha$ -naphthaflavone.** By E. KELLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 1034—1037).—Emilewicz and Kostanecki's method (*Abstr.*, 1898, i, 369) for the preparation of flavones applies also in the naphthalene series, since on condensing 2-acetyl-1-naphthol with anisaldehyde in the usual way, 2-anisylideneacetyl-1-naphthol,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , is formed as an orange-coloured substance crystallising from benzene or glacial acetic acid in needles melting at 158°. Its *acetyl* derivative crystallises in light yellow needles melting at 96°, and on bromination passes into the *dibromide* which separates from a mixture of chloroform and ether in white needles melting at 135.5°; this dibromide is converted by alcoholic potassium hydroxide into 4'-methoxy- $\alpha$ -naphthaflavone,



which crystallises in light yellow needles melting at 181°; its solution in strong sulphuric acid is yellow, with a green fluorescence.

4'-Methoxy- $\alpha$ -naphthaflavone is resolved by sodium ethoxide into 2-acetyl-1-naphthol and anisic acid, and on boiling for many hours with hydriodic acid gives the corresponding 4'-hydroxy- $\alpha$ -naphthaflavone, a colourless substance crystallising in needles melting at 315—316°; it dissolves in sodium hydroxide solution with a yellow colour, and behaves towards sulphuric acid in the same way as the methylic ether. 4'-Acetoxy- $\alpha$ -naphthaflavone crystallises from glacial acetic acid and alcohol in white needles melting at 215°. J. F. T.

**2'-Ethoxy- $\alpha$ -Naphthaflavone.** By D. ALPERIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 1037—1039. Compare preceding abstract).—*Orthethoxy-2-benzylideneacetyl-1-naphthol* crystallises from

glacial acetic acid in orange-red needles melting at 154—155°, which are coloured red by concentrated sulphuric acid; the *acetyl* derivative crystallises in light orange leaflets melting at 125—126°, and the *dibromide* in colourless prisms melting at 155—156°. 2'-*Ethoxy-a-naphthaflavone* separates from alcohol in pale yellow needles melting at 160°, and dissolves in concentrated sulphuric acid to a light orange solution showing an intense green fluorescence; it is decomposed by sodium ethoxide into acetylnaphthol and salicylic acid.

Furfuraldehyde combines with 2-acetyl-1-naphthol, forming 2-furfurylideneaceto-1-naphthol,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_4\text{H}_3\text{O}_2$ , which crystallises in red needles or leaflets melting at 121—122°; the *acetyl* derivative separates from alcohol in yellow plates melting at 116—117°, but on bromination does not yield the desired dibromide. J. F. T.

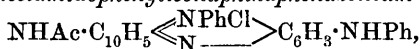
**The Seventh Isomeride of Rosinduline.** By FRIEDRICH KEHRMANN and M. RAVINSON (*Ber.*, 1899, 32, 927—932. Compare *Abstr.*, 1898, i, 155; and this vol., i, 235 and 238).—2"-*Acetamidophenylisonaphthaphenazonium chloride*,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_5 \llcorner \text{NPhCl} \gg \text{C}_6\text{H}_4$ ,

is formed when orthamidodiphenylamine hydrochloride dissolved in the smallest possible quantity of alcohol to which a few drops of hydrochloric acid have been added, is mixed with 3'-acetamido-1:2-naphthaquinone suspended in alcohol and the mixture warmed on the water-bath to the boiling point of the alcohol; when purified by solution in water and precipitation with hydrochloric acid, it forms orange-yellow, crystalline nodules with a green, metallic lustre; its alcoholic solution exhibits an orange-red colour with a distinct yellow fluorescence. The *platinochloride*,  $(\text{C}_{24}\text{H}_{17}\text{N}_3\text{O})_2 \cdot \text{H}_2\text{PtCl}_6$ , forms a brick-red, crystalline powder, and the *dichromate*,  $(\text{C}_{24}\text{H}_{18}\text{N}_3\text{O})_2 \cdot \text{Cr}_2\text{O}_7$ , crystallises in small, brownish-red plates.

2"-*Amidophenylisonaphthaphenazonium chloride*,  $\text{C}_{22}\text{H}_{16}\text{N}_3\text{Cl}$ , obtained when the acetyl derivative is warmed with dilute hydrochloric acid until the solution assumes a pure violet colour, is precipitated by the addition of solid sodium chloride and purified by crystallisation from very dilute hydrochloric acid, and thus forms dark violet, laminated plates with a coppery lustre. Its aqueous and alcoholic solutions are pure violet in colour and exhibit no fluorescence; its *platinochloride* forms a violet-coloured, lustrous precipitate. The above chloride is the seventh isomeride of rosinduline which has been prepared; its constitution as a phenylisonaphthaphenazonium derivative follows from the fact that, when the amido-group is eliminated, phenylisonaphthaphenazonium is obtained.

Isorosinduline No. 7 does not react with amines, but its acetyl derivative forms condensation products with aniline or ammonia, the hydrogen in the para-position (3) to the azine nitrogen atom becoming replaced by  $\text{NH}_2$  and  $\text{NHPh}$  respectively.

3-*Anilido-2"-acetamidophenylisonaphthaphenazonium chloride*,



is readily formed when an alcoholic solution of the chloride of the acetyl derivative is allowed to remain in contact with an excess of

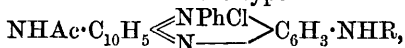
aniline and the theoretical amount of aqueous sodium hydroxide for 24 hours and the product then acidified with hydrochloric acid; after recrystallisation from boiling alcohol, it forms a microcrystalline powder with a coppery lustre, is only sparingly soluble in water, somewhat more readily in hot alcohol or acetic acid, yielding bluish-black solutions.

The *hydroxide*,  $C_{30}H_{24}N_4O_2$ , is obtained in the form of a black, crystalline powder when an alcoholic solution of the chloride is treated with water and a slight excess of sodium carbonate. When the chloride is hydrolysed with hydrochloric acid and alcohol, 3-*anilido*-2''-*amidophenylisonaphthaphenazonium chloride* is obtained in the form of needles having a coppery lustre; it dissolves in water or alcohol, yielding blue solutions, and its *platinochloride*,  $(C_{28}H_{20}N_4)_2 \cdot H_2PtCl_6$ , forms a blue, crystalline powder.

3-*Amido*-2''-*acetamidophenylisonaphthaphenazonium chloride*, obtained by the action of an excess of ammonia on the chloride of acetylrosinduline No. 7, crystallises from alcohol in dark-red crystals with a brassy lustre; its aqueous and alcoholic solutions have a dark blood-red colour and a fiery red fluorescence. When hydrolysed with hydrochloric acid, it yields 3:2''-*diamidophenylisonaphthaphenazonium chloride* in the form of metallic green crystals, which dissolve in water or alcohol with a pure violet, and in concentrated sulphuric acid with a reddish-brown, colour. The *platinochloride*,  $(C_{22}H_{16}N_4)_2 \cdot H_2PtCl_6$ , forms a dark violet, crystalline powder practically insoluble in water.

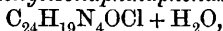
J. J. S.

**Action of Amines on Salts of 3'-Acetamidophenylisonaphthaphenazonium.** By FRIEDRICH KEHRMANN and WALTHER AEBI (*Ber.*, 1899, 32, 932—938).—Amines readily react with salts of 3'-acetamidophenylisonaphthaphenazonium (*Abstr.*, 1896, i, 509), yielding substituted derivatives of the type



in which the amido- or substituted amido-group occupies the position 2; when these are hydrolysed, the corresponding 2:3'-diamido-derivatives are obtained, which are characterised by the readiness with which the amido-group in the position 3' can be replaced.

2-*Amido*-3'-*acetamidophenylisonaphthaphenazonium chloride*,



obtained by alternately saturating an alcoholic solution of the 3'-acetamido-compound with ammonia and then removing the excess of ammonia by a current of air, is precipitated by the addition of dilute hydrochloric acid to its aqueous solution in the form of reddish-violet needles with a metallic lustre; its alcoholic solution has a red fluorescence, and that in concentrated sulphuric acid a dirty violet colour. The *nitrate* forms reddish-violet needles sparingly soluble in water, and the *platinochloride* brownish-red needles practically insoluble in water. 2:3'-*Diamidophenylisonaphthaphenazonium chloride*,  $C_{22}H_{17}N_4Cl + H_2O$ , obtained by carefully hydrolysing the acetamido-derivative with sulphuric acid and water, precipitating with sodium chloride, and crystallising from water containing a little hydrochloric acid, forms



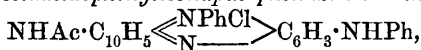
greenish-blue needles with a steely lustre, and is readily soluble in alcohol and hot water; its *platinochloride* is a black, crystalline powder practically insoluble in water. It is impossible to avoid the formation of 2-amido-3'-hydroxyphenylisonaphthaphenazonium during the hydrolysis; this is, however, precipitated as its *sulphate* in the form of dark blue needles, and dissolves fairly readily in water to a bluish-violet solution. The sulphate is most readily obtained by boiling the diamine with dilute sulphuric acid for half an hour; ammonia decomposes it into an anhydride of the base, namely, 2-amidonaphtha-

*prasindone*,  $\text{O} \left\langle \begin{array}{c} \text{NPh} = \text{C}_{16}\text{H}_3 \cdot \text{NH}_2 \\ \text{C}_{10}\text{H}_5 \cdot \text{N} \end{array} \right\rangle$ , which forms bluish-green needles soluble in boiling water or concentrated sulphuric acid.

2-Dimethylamido-3'-acetamidophenylisonaphthaphenazonium chloride,  $\text{C}_{26}\text{H}_{23}\text{N}_4\text{OCl}$ , after purification by repeated solution in water, filtration, and precipitation with hydrochloric acid, forms blue needles which contain  $1\text{H}_2\text{O}$ , even when dried at  $150^\circ$ ; the *nitrate*,  $\text{C}_{26}\text{H}_{23}\text{N}_4\text{O} \cdot \text{NO}_3 + \text{H}_2\text{O}$ , crystallises in glistening, blue needles sparingly soluble in water; the *platinochloride* forms slender, blue needles insoluble in water, and the *aurichloride* a dark blue, flocculent precipitate.

2-Dimethylamidonaphthaprasindone sulphate crystallises from its hot aqueous sulphuric acid solution in dark greenish-blue needles with a coppery lustre; when boiled with water, it undergoes dissociation, and the *prasindone* is precipitated; this is more readily obtained by the action of ammonia on the sulphate, and forms light, pale green needles insoluble in water.

2-Anilido-3'-acetamidophenylisonaphthaphenazonium chloride,



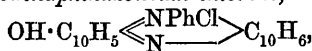
crystallises in coppery plates practically insoluble in cold water, but dissolving in alcohol to a dark blue solution; when treated with sodium carbonate, it yields an *anhydride*,  $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}$ , in the form of slender, dark blue needles; this anhydride must have either a *prasindone* or *rosindone* constitution. The *nitrate*,  $\text{C}_{30}\text{H}_{23}\text{N}_4\text{O} \cdot \text{NO}_3$ , forms slender, blue needles insoluble in water; the *platinochloride*,  $(\text{C}_{30}\text{H}_{22}\text{N}_4\text{O})_2 \cdot \text{H}_2\text{PtCl}_6$ , in microscopic crystals, and the *aurichloride*,  $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O} \cdot \text{HAuCl}_4$ , have been prepared. J. J. S.

**Naphthindulines and Naphthazonium Compounds.** By FRIEDRICH KEHRMANN and W. F. SUTHERST (*Ber.*, 1899, 32, 939—947). —An acetic acid solution of 4-acetamido-1 : 2-naphthaquinone (*Abstr.*, 1895, i, 151) readily condenses with phenylorthonaphthylenediamine hydrochloride (*Abstr.*, 1887, 590), yielding a mixture of two isomeric chlorides,  $\text{C}_{28}\text{H}_{20}\text{N}_3\text{OCl}$ . The one, 4-acetamidophenylidinaphthazonium chloride,  $\text{NHAc} \cdot \text{C}_{10}\text{H}_5 \left\langle \begin{array}{c} \text{N} \\ \text{NPhCl} \end{array} \right\rangle \text{C}_{10}\text{H}_6$ , is sparingly soluble in acetic acid and the greater part crystallises out after the mixture has been kept for 4 days at the ordinary temperature; it may be purified by crystallisation from boiling alcohol, and is thus obtained in the form of brick-red needles with a green, metallic lustre; its solutions, especially

in dilute alcohol, exhibit a strong, orange-yellow fluorescence. The *nitrate*,  $C_{23}H_{20}N_3O \cdot NO_3$ , forms brick-red needles sparingly soluble in water; the *platinochloride*, glistening, golden-red plates, and the *dichromate*, an insoluble crystalline precipitate. When an alcoholic solution of the sparingly soluble chloride is boiled with dilute sulphuric acid, the greater part of the alcohol distilled off, and sodium chloride added, *amidophenylidinaphthazonium chloride* is obtained; this crystallises from alcohol in dark-red, glistening needles sparingly soluble in water, alcohol, or acetic acid. The *nitrate* is also sparingly soluble in water and crystallises in metallic green needles. These salts are identical with those obtained from Fischer and Hepp's so-called naphthinduline (Abstr., 1893, i, 333). The base melts at  $253-255^\circ$  (according to Fischer and Hepp, at  $248-250^\circ$ ). It is undoubtedly an azonium compound, and is to be regarded as the "rosinduline" of dinaphthazonium, since, when the amido-group is eliminated, salts of phenyldinaphthazonium are obtained. *Phenyldinaphthazonium chloride*,  $C_{10}H_6 \llbracket \begin{smallmatrix} N \\ \text{NPhCl} \end{smallmatrix} \rrbracket C_{10}H_6$ , crystallises from alcohol in reddish-brown, glistening needles, and is sparingly soluble in water, the solution exhibiting a strong, yellowish-green fluorescence. The *nitrate* is precipitated from an aqueous solution of the chloride by dilute nitric acid; the *platinochloride* crystallises in golden-brown, glistening plates.

The more soluble of the two isomeric chlorides, 4-acetamidophenylisodinaphthazonium chloride,  $NHAc \cdot C_{10}H_5 \llbracket \begin{smallmatrix} 1,2 \\ \text{NPhCl} \end{smallmatrix} \rrbracket^{3,4} C_{10}H_6$ , crystallises from alcohol in brick-red, felted needles, and is fairly readily soluble in water or acetic acid, yielding dark-red solutions which are not fluorescent; the *nitrate* forms dark-red needles practically insoluble in water, and the *dichromate* a violet-red powder. *Amidophenylisodinaphthazonium chloride*, obtained by hydrolysing the acetamido-compound with sulphuric acid and precipitating with sodium chloride, crystallises from alcohol in green needles soluble in alcohol to a bluish-green and in water to a violet-blue solution. The *nitrate* crystallises in bluish-green needles very sparingly soluble in water.

4-Hydroxyphenylisodinaphthazonium chloride,



obtained by boiling the amido- or acetamido-derivative with an excess of sulphuric acid, dissolving the hydroxy-sulphate thus formed in water, and precipitating with hydrochloric acid, forms chocolate-coloured needles; the *nitrate* crystallises in violet-brown needles. The base appears to exist only in the form of an anhydride, *dinaphthaprasindone*,

$O \llbracket \begin{smallmatrix} \text{NPh} \\ \text{C}_{10}H_5 \cdot \text{N} \end{smallmatrix} \rrbracket C_{10}H_6$ , and crystallises from alcohol in bluish-green, glistening plates; when treated with acetic anhydride, it forms an *acetyl*

derivative, which yields a *nitrate*,  $OAc \cdot C_{10}H_5 \llbracket \begin{smallmatrix} \text{NPh}(\text{NO}_3) \\ \text{N} \end{smallmatrix} \rrbracket C_{10}H_6$ , crystallising from alcohol or ether in brassy, brown-red plates readily soluble in water or alcohol, and a *platinochloride*, forming golden-red, glistening plates insoluble in water.

J. J. S.

**Action of some Copper Salts on  $\beta$ -Naphthol.** By R. FOSSE (*Bull. Soc. Chim.*, 1898, [iii], 19, 610—611).— $\beta$ -Naphthol is oxidised by cupric acetate, formate, chloride, or nitrate in boiling aqueous solution with the formation of  $\beta\beta$ -dinaphthol. The addition of a little ammonia favours oxidation by neutralising the acid liberated in the reaction. Cupric sulphate and potassium cupric tartrate are without action on  $\beta$ -naphthol.  $\alpha$ -Naphthol is distinguished from  $\beta$ -naphthol by yielding, under the same conditions, a deep violet precipitate which could not be obtained in a crystalline form. N. L.

**Action of Ethylenic Bromide on  $\beta\beta$ -Dinaphthol.** By R. FOSSE (*Bull. Soc. Chim.*, 1898, [iii], 19, 611—612).—When  $\beta\beta$ -dinaphthol is heated at  $150^\circ$  with alcoholic potash and ethylenic bromide, *dinaphthyl ethylenic ether*,  $C_{20}H_{12} \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}$ , is formed; it is crystalline and melts at  $196$ — $197^\circ$ . N. L.

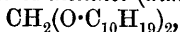
**Action of Methylenic Chloride on  $\beta\beta$ -Dinaphthol.** By R. FOSSE (*Bull. Soc. Chim.*, 1898, [iii], 19, 612).—When a mixture of  $\beta\beta$ -dinaphthol with methylenic chloride and alcoholic potash is heated in a sealed tube, *dinaphthyl methylenic ether*,  $C_{20}H_{12} \begin{smallmatrix} \diagup O \diagdown \\ \diagdown O \diagup \end{smallmatrix} CH_2$ , is obtained; it does not crystallise well.

The *diacetate* of  $\beta\beta$ -dinaphthol,  $C_{20}H_{12}(OAc)_2$ , melts at  $109^\circ$ , is soluble in alcohol and ether, insoluble in alkalis, and gives a rose coloration with sulphuric acid. N. L.

**Constitution of Terpenes and Allied Compounds.** By K. ŚLAWINSKI (*Chem. Centr.*, 1898, ii, 543—544; from *J. Russ. Chem. Soc.*, 1898, 30, 195—214).—The pinolglycol prepared from dibromopinol and that obtained by oxidising pinol with potassium permanganate are stereoisomerides. The latter boils at  $281$ — $282^\circ$ , is easily soluble in water, alcohol, ether, or glacial acetic acid, and slightly in light petroleum; it crystallises from water in monoclinic plates melting at  $128$ — $129^\circ$ , from ethylic acetate in rhombic prisms melting at  $126$ — $127^\circ$ , and when sublimed forms thin leaflets which melt at  $128.5$ — $129.5^\circ$ . The acetyl derivative,  $C_{10}H_{16}O(OAc)_2$ , prepared by heating with acetic anhydride, is a thick, optically inactive syrup, slightly soluble in water, boils at  $165$ — $167^\circ$  under 17 mm. pressure, and has a sp. gr. 1.1360 at  $20^\circ/20^\circ$ ; when hydrolysed, it yields the original glycol melting at  $128$ — $129^\circ$ , and when heated with phenylcarbimide forms a mixture of mono- and di-urethanes which melts at  $151$ — $154^\circ$ . The acetyl derivative,  $C_{10}H_{16}O(OAc)_2$ , obtained from silver acetate, glacial acetic acid, and dibromopinol, melts at  $97^\circ$ , boils at  $151$ — $152^\circ$  under 8.5 mm. pressure, and yields Wallach's pinene glycol, which melts at  $123$ — $124^\circ$  and boils at  $158$ — $159^\circ$  under 12 mm. pressure. Wallach's acetyl derivative melts at  $97^\circ$  and boils at  $151$ — $152^\circ$  under 85 mm. pressure, whilst Wagner's pinolglycol from pinol melts at  $128.5$ — $129^\circ$ , boils at  $157$ — $158^\circ$  under 12 mm. pressure, and yields a liquid acetyl derivative which boils at  $154$ — $155^\circ$  under 10.5 mm. pressure. The glycols prepared from the acetyl derivatives, when oxidised with a 5 per cent. solution of potassium permanganate (4 mols. oxygen to 1

mol. glycol), yield acetic and terpenylic acids, and in one experiment the liquid glycol gave a little terebic acid. The reactions of the glycols indicate the same structural formula, and the method of formation of sobrerol from pinol by means of the additive bromine compound,  $C_{10}H_{16}(OH)_2Br_2$ , shows that the OH-groups are in the *cis*-position and hence the oxides, when hydrogenised, form the *cis*-glycol identical with that from dibromopinol. The author combats Ginzberg's views (*J. Russ. Chem. Soc.*, 29, 267), and considers his formula for sobreritol unsatisfactory. Pinene glycol is a partial anhydride of the tetrahydric sobreritol, and hence may be considered as a dihydric alcohol of the  $\alpha$ - and an oxide of the  $\gamma$ -series. This combination of a secondary and tertiary alcohol with an oxide confers characteristic properties on the glycol and its derivatives: thus dibromopinol loses its bromine even by the action of silver nitrate in alcoholic solution, but does not readily yield hydrogen bromide; the acetyl derivatives also are extremely easily hydrolysed. The glycol does not lose water at  $150^\circ$ , but by the action of 2 per cent. hydrochloric acid solution, water is removed and an unsaturated compound formed. The similarity of the reactions of the polymethylene compounds and the aliphatic glycols is pointed out, thus trimethylethylenic glycol, by the action of acetic anhydride, yields unsaturated compounds and the acetyl derivative,  $C_5H_{10}(OAc)_2$ .  
E. W. W.

**Action of Formaldehyde on Menthol and Borneol.** By ANDRÉ BROCHET (*Compt. rend.*, 1899, 128, 612—613. Compare this vol., i, 376).—The *methylenic acetal* of *menthol* (*dimentholic formal*),



obtained by the condensation of menthol with formaldehyde in the presence of mineral acids, crystallises from alcohol in colourless, silky needles, melts at  $56.5^\circ$ , and boils with slight decomposition at  $337^\circ$  under ordinary pressure. It has a disagreeable odour, unlike that of menthol, and may be distilled without alteration under reduced pressures.

The *methylenic acetal* of *borneol* (*diborneolic formal*),  $CH_2(O \cdot C_{10}H_{17})_2$ , crystallises from alcohol in nacreous lamellæ, melts at  $166^\circ$ , and distils unchanged at  $344$ — $345^\circ$  under ordinary pressure. It is very soluble in the ordinary organic solvents, and has an odour resembling that of borneol, which is not removed by repeated crystallisation and distillation. These substances are not hydrolysed by water or a 15 per cent. solution of sodium hydroxide even at  $150^\circ$ .

The corresponding derivatives of linalool and geraniol could not be obtained owing to the action of the mineral acid on these alcohols.

G. T. M.

**Terpenes and Ethereal Oils. The Carvone Series.** By OTTO WALLACH (*Annalen*, 1899, 305, 223—259).—[With H. LÖHR and E. LIPCZYNSKI].—The compound,  $C_{20}H_{30}O_2$ , produced along with dihydrocarvone when carvone is reduced with alcohol and sodium (Wallach and Schrader, *Abstr.*, 1894, i, 537), is not a pinacone, but a ketone, *dicarvelone*. It has been obtained in nine forms, of which the  $\alpha$ -modifications are obtained from carvone by the action of alcoholic potash and zinc dust, and give rise to the  $\beta$ -isomerides when the hydrobromides are treated with alcoholic potash; the  $\gamma$ -modifications

are obtained when the other forms are dissolved in concentrated sulphuric acid.

$\alpha$ -Dl-Dicarvelone melts at 148—149°, and has the specific rotatory power  $[\alpha]_D = -73.9^\circ$ .  $\alpha$ -Ld-Dicarvelone has  $[\alpha]_D = +73.2^\circ$ .  $\alpha$ -i-Dicarvelone, prepared by mixing equal weights of the foregoing modifications, also crystallises in the rhombic system and melts at 120—121°; the *phenylhydrazone* decomposes at about 200°, whilst the corresponding derivative of the active ketones melts at 215°. The active *dioxime* melts at 223°, and yields a *diacetyl* derivative melting at 187°; the derivatives of the racemic ketone melt at 287° and 166° respectively. The *dihydrobromide* of  $\alpha$ -Dl-dicarvelone separates from alcohol in white crystals and melts at 165°.

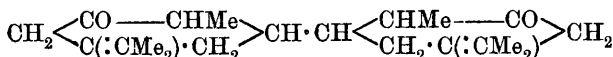
$\beta$ -Dd-Dicarvelone, prepared from  $\alpha$ -Dl-dicarvelone, melts at 207°, and has the specific rotatory power  $[\alpha]_D = +79.1^\circ$ .  $\beta$ -Ll-Dicarvelone, obtained from  $\alpha$ -Ld-dicarvelone, has  $[\alpha]_D = -82.6^\circ$ .  $\beta$ -i-Dicarvelone melts at 168°.

$\gamma$ -Dl-Dicarvelone, derived from  $\alpha$ -Dl-dicarvelone, melts at 126°, and has the specific rotatory power  $[\alpha]_D = -213.4^\circ$ ;  $\gamma$ -Dl-dicarvelone, prepared from  $\beta$ -Dd-dicarvelone, has  $[\alpha]_D = -201.8^\circ$ .  $\gamma$ -Ld-Dicarvelone has  $[\alpha]_D = +236.8^\circ$ .  $\gamma$ -i-Dicarvelone melts at 112°.

The constitution of  $\alpha$ -dicarvelone and  $\beta$ -dicarvelone are represented by the formulæ



and



respectively.

*Dieucarvelone*,  $\text{C}_{20}\text{H}_{30}\text{O}_2$ , obtained by reducing eucarvone, carvone hydrochloride, or carvone hydrobromide with alcoholic potash and zinc dust, occurs in two modifications, which melt at 172° and 128° respectively.

[With H. LÖHR.]—Eucarvone (von Baeyer, Abstr., 1894, i, 298) boils at 104—106° under 20 mm. pressure, and has a sp. gr. 0.952 at 20°, and a refractive index  $n_D$  1.5048, whence  $M = 46.72$ .

Dihydroeucarvylamine,  $\text{C}_{10}\text{H}_{17}\cdot\text{NH}_2$ , prepared by reducing the oxime in alcoholic solution with sodium, boils at 116—117° under a pressure of 40 mm. (von Baeyer, Abstr., 1895, i, 152); the *phenylcarbamide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_{17}$ , melts at 142°, and the *phenylthiocarbamide* crystallises from methylic alcohol in transparent plates and melts at 120—121°.

The compound,  $\text{C}_{24}\text{H}_{24}\text{O}_2$ , melting at 193—194°, is produced along with benzylidene-eucarvone when the ketone is condensed with benzaldehyde (Abstr., 1896, i, 573); its constitution is probably represented

by the formula  $\text{C}_7\text{H}_{10} \begin{array}{c} \text{CH} \cdot \text{CHPh} \\ \text{>CO} \\ \text{CH} \cdot \text{CHPh} \end{array} \text{O}$  (compare Vorländer, Abstr.,

1898, i, 27).

[With C. OHLIGMACHER.]—The base,  $\text{C}_{10}\text{H}_{15}\text{NO}$ , obtained by the action of ammonia on racemic carvone tribromide (Abstr., 1895,

i, 622), yields an *oxime*,  $\text{OH} \cdot \text{C}_{10}\text{H}_{13} \cdot \text{NOH}$ , which crystallises from water in needles and melts at  $100^\circ$ ; when the hydrochloride of the base is submitted to dry distillation, the compound  $\text{C}_{10}\text{H}_{15}\text{NO}$  is formed, which melts at  $165\text{--}167^\circ$ .

*Di-Carvenolide*,  $\text{C}_{10}\text{H}_{14}\text{O}_3$ , is the lactone corresponding with the base derived from *d*-carvone, and melts at  $41\text{--}42^\circ$  (compare Abstr., 1895, i, 622); it has the specific rotatory power  $[\alpha]_D = -138.5^\circ$ , and the *dibromide*, which melts at  $97\text{--}99^\circ$ , has  $[\alpha]_D = -67.0^\circ$ . *Ld-Carvenolide* has  $[\alpha]_D = +143.3$ . *i-Carvenolide* melts at  $71\text{--}72^\circ$ ; the *dibromide* melts at  $95\text{--}96^\circ$ .

*Dd-Carvenolic acid*,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , obtained by the action of alcoholic sodium methoxide on the lactone from *d*-carvone, melts at  $133^\circ$ , and has the specific rotatory power  $[\alpha]_D = +178.7^\circ$ . *i-Carvenolic acid* melts at  $135\text{--}136^\circ$ .

The *acid*,  $\text{C}_7\text{H}_{10}\text{O}_2$ , produced on heating carvenolic acid with potash at  $230\text{--}250^\circ$ , melts at  $130\text{--}131^\circ$ , and is volatile in steam. The *dibromide*,  $\text{C}_7\text{H}_{10}\text{Br}_2\text{O}_2$ , melts and decomposes at  $150^\circ$ . Chromic and nitric acids oxidise carvenolic acid, forming the *acid*  $\text{C}_7\text{H}_{10}\text{O}_4$ , which melts at  $201\text{--}202^\circ$ .

Constitutional formulæ representing the foregoing substances are suggested. M. O. F.

**Terpenes and Ethereal Oils. Condensation of Benzaldehyde with Ketones of the Terpene Series.** By OTTO WALLACH [and MILO C. BURR] (*Annalen*, 1899, 305, 261—276).—Benzylidenementhone is the condensation product obtained from benzaldehyde and menthone (Abstr., 1896, i, 573). *Benzylmenthol*,  $\text{OH} \cdot \text{C}_{10}\text{H}_{18} \cdot \text{CH}_2\text{Ph}$ , obtained by reducing benzylidenementhone, crystallises from ether, and melts at  $111\text{--}112^\circ$ ; it boils at  $181\text{--}183^\circ$  under 10 mm. pressure. *Methylisopropylhexahydrofluorene*,  $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPr}^s \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \end{array}$ , produced by the

action of phosphoric anhydride on benzylmenthol, is a colourless liquid which boils at  $153\text{--}155^\circ$  under 10 mm. pressure; it does not decolorise a cold solution of potassium permanganate. *Benzylidenementhylamine*,  $\text{C}_{17}\text{H}_{25}\text{N}$ , formed on reducing benzylidenementhone-oxime in alcoholic solution with sodium, boils at  $200\text{--}205^\circ$  under 10 mm. pressure.

When dried hydrogen chloride is passed into a mixture of benzaldehyde and tetrahydrocarvone, the compound  $\text{C}_{24}\text{H}_{28}\text{O}_2$  is produced; it crystallises from ethylic acetate and melts at  $175^\circ$ .

*Benzylpulegol*,  $\text{OH} \cdot \text{C}_{10}\text{H}_{16} \cdot \text{CH}_2\text{Ph}$ , obtained by reducing benzylidenepulegone, is a viscous oil which boils at  $192\text{--}195^\circ$  under 10 mm. pressure; the *hydrocarbon*,  $\text{C}_{17}\text{H}_{22}$ , formed by the action of phosphoric anhydride, boils at  $162\text{--}164^\circ$  under 10 mm. pressure.

*Benzylidenedihydrocarvone*,  $\text{C}_{10}\text{H}_{14}\text{O} \cdot \text{CHPh}$ , boils at  $187\text{--}190^\circ$  under 10 mm. pressure; the *oxime* crystallises from methylic alcohol in colourless needles and melts at  $145\text{--}146^\circ$ . *Benzylidihydrocarvol*,  $\text{OH} \cdot \text{C}_{10}\text{H}_{16} \cdot \text{CH}_2\text{Ph}$ , boils at  $182\text{--}183^\circ$  under 10 mm. pressure; the *hydrocarbon*,  $\text{C}_{17}\text{H}_{22}$ , obtained by the action of phosphoric anhydride, boils at  $166\text{--}169^\circ$  under 10 mm. pressure.

Carvenone resembles tetrahydrocarvone in its behaviour towards

benzaldehyde, yielding the compound  $C_{24}H_{26}O_2$ , in which the ketone is combined with 2 molecular proportions of the aldehyde; it crystallises from methylic alcohol, and melts at  $170-171^\circ$ . Menthone gives rise to the compound  $C_{24}H_{24}O$ , which crystallises from alcohol in slender, pale yellow needles melting at  $129-130^\circ$ ; reduction with zinc dust and acetic acid transforms it into the compound  $C_{24}H_{26}O$ , which melts at  $72-75^\circ$ .

A table comparing the physical properties of isomeric ketones,  $C_{10}H_{16}O$ , belonging to the terpene series is included in the paper.

M. O. F.

**Essential Oil of Caparrapi.** By F. J. TAPIA (*Bull. Soc. Chim.*, 1898, [iii], 19, 638—644).—Oil of caparrapi is a thick liquid, of acid reaction and sweet, agreeable odour, which exudes from incisions made in the capelo tree (*Nectandra caparrapi*) of Colombia. It varies in colour from pale yellow to dark brownish-red, and two varieties are recognised in commerce, the "white" oil and the "black." The former has a sp. gr. 0.9336 at  $15^\circ$  and a rotatory power  $-3^\circ$ ; when cooled to  $-27^\circ$ , it becomes turbid and semi-solid, and some specimens, when kept, deposit crystals of the acid described below. The black oil has a sp. gr. 0.9163 at  $15^\circ$ , is less viscid than the white, and remains fluid and transparent when cooled; both varieties are readily soluble in most organic solvents. From the white oil, by treatment with dilute aqueous soda or lime-water and subsequent acidification with hydrochloric acid, an acid,  $C_{15}H_{26}O_3$ , is obtained which crystallises in white needles, melts at  $84.5^\circ$ , has a rotatory power  $[\alpha]_D = +3^\circ$  in alcoholic solution, and is very slightly soluble in cold, rather more soluble in hot, water, and readily soluble in alcohol. The calcium salt,  $Ca(C_{15}H_{25}O_3)_2 + 5H_2O$ , crystallises in long, white, silky needles melting at  $250^\circ$ , and is very slightly soluble in cold water, very soluble in dilute, boiling alcohol. The silver, sodium, and ammonium salts are also crystalline. The white oil from which the acid has been extracted, when distilled with steam, yields a colourless, liquid, sesquiterpenic alcohol, *caparrapiol*,  $C_{15}H_{26}O$ ; it has a sp. gr. 0.9146, a rotatory power  $[\alpha]_D = -18.58^\circ$ , refractive index 1.4843, and boils at  $260^\circ$  under 757 mm. pressure. When distilled with phosphoric or acetic anhydride, it is converted into the corresponding hydrocarbon, *caparrapene*,  $C_{15}H_{24}$ , a colourless liquid which boils at  $240-250^\circ$  and has a sp. gr. 0.9019 at  $16^\circ$ , a rotatory power  $[\alpha]_D = -2.21^\circ$ , and refractive index 1.4953; its solution in acetic acid gives a rose coloration, changing to intense violet on the addition of a trace of sulphuric acid. The residue from the steam-distillation of the white oil, constituting nearly three-fourths of the whole, is a very thick, yellowish liquid of sp. gr. 0.9751 at  $18^\circ$ , and rotatory power  $[\alpha]_D = +3.33^\circ$ ; it contains oxygen.

The black oil, when treated with alkalis, yields a resinous acid of disagreeable odour which is not improbably a decomposition product of the crystalline acid contained in the light coloured oils. After removal of this acid, the oil has a sp. gr. 0.9319, a rotatory power  $[\alpha]_D = +6.43^\circ$ , and a refractive index 1.4811; on distillation, it yields 35.8 per cent. of caparrapiol.

N. L.

**Essential Oil of Cochlearia Officinalis.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 92—105. Compare Hofmann, *Abstr.*, 1874, 792).—The dried plant (*sine floribus*) was cut up, macerated with water, with the addition of 1/5 of its weight of flour of white mustard, and distilled with superheated steam; from 28 kilos. of the dried scurvy grass, 66 grams of oil were obtained. From a sample of the green plant, no oil could be obtained, but the plant had already flowered, and fermentation had set in by the time it was received. The oil boiled at 150—162°, and the two fractions, boiling at 150—154° and 154—156°, were found to be the purest, being practically pure secondary butylthiocarbimide,  $C_4H_9NCS$ ; they had respectively the sp. gr. 0.94328 and 0.94279 at 20°/20°, molecular rotation  $[M]_D = +59.12^\circ$  and  $+61.15^\circ$ , and index of refraction 1.4923 and 1.4925 at 22°. The amount of thiocarbimide was estimated by dissolving a weighed quantity of the oil in alcohol, adding excess of N/10 silver nitrate solution, allowing the whole to remain for 24 hours in a well-stoppered bottle, filtering from the precipitated silver sulphide, and titrating the excess of silver with ammonium thiocyanate solution. The fractions of the oil of higher boiling point had a rather larger rotation and lower sp. gr.; possibly they contained a little *d*-limonene.

Secondary butylthiocarbamide,  $NH_2 \cdot CS \cdot NH \cdot C_4H_9$ , obtained by treating the oil with ammonia, forms monoclinic crystals, and at 20° has a molecular rotation  $[M]_D = +30.06^\circ$  to  $30.27^\circ$  in alcoholic solution of about 3.5 per cent. strength, and  $44.15^\circ$  in 1 per cent. aqueous solution. When the oil is heated with twice its volume of water for 8—10 hours at 200°, a little secondary butylamine is formed, but the main product is a *d,d*-dibutylthiocarbamide,  $CS(NH \cdot C_4H_9)_2$ , in which both the secondary butyl groups are dextrorotatory; this melts at 108—110°, and has a molecular rotation  $[M]_D = +77.08^\circ$  at 17° in 3.3 per cent. alcoholic solution. The *r,d*-isomeride, obtained by the action of inactive, or racemic, secondary butylamine on active secondary butyl thiocarbamide, melts at 102—102.5°, and has a molecular rotation  $[M]_D = +34.84^\circ$  under the same circumstances, being considerably less than half the value when both butyl groups are optically active.

The further action of water on the *d,d*-compound produces secondary butylamine; the compound is heated with 5 times its weight of water for 15 hours at 200°—for a time at 240°. This amine is optically inactive; attempts to decompose it into its active components have been hitherto unsuccessful. Two *aurichlorides* were obtained from it, however; the less soluble crystallises with  $1H_2O$  and melts at 50—52°, when anhydrous at 110°; the other forms anhydrous crystals and melts at about 150°.

C. F. B.

**Essential Oils of Geranium, Citronella, and Roses.** By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 635—636).—The geraniol and citronellol in (1) Indian geranium oil, (2) Réunion geranium oil, (3) rose oil, and (4) citronella oil have been determined by the method previously described (*Abstr.*, 1898, i, 618), with the following results:—

	1.		2.		3.		4.
Geraniol, per cent. ...	63	...	70	...	70	...	40
Citronellol     ,,     ...	11	...	10	...	15	...	6

N. L.



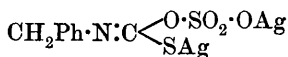
**Essential Oil of Melissa.** By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 636—637).—A specimen of oil of melissa (balm) was found to contain 20 per cent. of geraniol, 12 per cent. of linalool, and about 6 per cent. of citronellol. N. L.

**Essential Oil of Origanum Majorana.** By WILHELM BILTZ (*Ber.*, 1899, 32, 995—999).—The crude oil used in the research had a sp. gr. 0.898 at 14°/14°, a refractive index  $n_D$  1.47738 at 14.5°, and rotation  $\alpha_D = +15^\circ 45'$  (100 mm.) at 15°. Fractional distillation under reduced pressure gave a fraction boiling at 77—81° under 30 mm. pressure and having the composition  $C_{10}H_{16}$ , whilst the last fraction boiled at 117—119° under 30 mm. pressure and had the composition  $C_{10}H_{18}O$ ; the remaining fractions were intermediate in composition and in boiling point. The terpene fractions, when distilled from sodium, boiled at 64—74° under 20 mm. pressure, and were found to consist largely of terpinene, which was identified by the formation of the nitrosite; a determination of the molecular weight of the fractions of highest boiling point showed that sesquiterpenes were not present in any large quantity; about two-fifths of the oil consists of terpenes. The presence of terpineol was shown by oxidation, when Wallach's trihydroxyhexahydrocymene,  $C_{10}H_{17}(OH)_3$ , and the ketolactone,  $C_{10}H_{16}O_3$ , were isolated (*Abstr.*, 1893, i, 597). Hydrolysis with potassium hydroxide showed the presence of 6 per cent. of ethereal salts reckoned as terpinyl acetate and the characteristic odour of the oil disappeared. The presence of acetic acid was proved, but other acids also appear to be present. T. M. L.

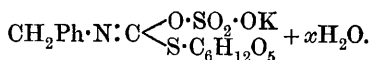
**Essential Oil of Tropæolum Majus.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 111—120).—When this plant, in the green state, is minced in a mincing machine and distilled with steam in a vessel which may be of metal provided that it is well-tinned inside, an oil can be extracted from the distillate with ether, and this oil is benzylthiocarbimide, as it has the smell characteristic of thiocarbimides, and yields benzylthiocarbamide when it is dissolved in alcohol and treated with 30 per cent. ammonia. From 14 kilos. of the plant, 5 grams of oil, containing 86 per cent. of benzylthiocarbimide, were obtained. Hofmann (*Abstr.*, 1874, 793) did not obtain any thiocarbimide, but benzylic cyanide instead; this is probably because he distilled the plant without crushing it first, and the thiocarbimide is formed only by the action of an enzyme on a glucoside, contained in different cells of the plant; the enzyme was destroyed before it could act on the glucoside, and the latter then yielded benzylic cyanide as a product of decomposition.

Attempts to isolate the glucoside have been so far successful that a neutral aqueous solution of it, almost free from foreign matter, has been obtained. On the addition of silver nitrate to this solution, a white precipitate is formed and the solution becomes acid; the precipitate dissolves in ammonia, but crystals of a compound,  $CH_2Ph \cdot NCS, Ag_2SO_4, 2NH_3$ , separate almost immediately from the solution. (This is quite analogous to what happens with the glucosides of black and white mustard; *Abstr.*, 1897, i, 254, 360). Hydrochloric acid decomposes the silver precipitate, forming silver

chloride, sulphur, and benzylic cyanide. To it and the hypothetical glucoside the following formulæ are assigned :—



Silver salt (tropæolate).



Glucoside (glucotropæolin).

The author proposes that this glucoside should be named *glucotropæolin*, that the monobasic acids of which this and the sinigrin and sinalbin of black and white mustard are the salts should be called glucotropæolic, glucosinigrin and glucosinalbinic acids respectively, whilst to the dibasic acids obtained from these by the loss of glucose the names tropæolic, sinigrin, and sinalbinic acids are assigned.

C. F. B.

**Empyreumatic Oil of Juniper.** By CATHELINEAU and JEAN HAUSSE (Bull. Soc. Chim., 1898, [iii], 19, 577—580).—From 400 c.c. of empyreumatic oil of juniper, by treatment with 5 per cent. aqueous soda, followed by various processes of extraction and distillation which are described in detail in the paper, the following products were obtained: *Soluble in soda*.—Extracted by light petroleum, 9 c.c.; extracted by amyl alcohol, 36 grams; oil volatile with steam, 6 c.c.; resin, 19 grams; soluble oil not volatile with steam, 4 c.c.; soluble acids volatile with steam, 3 c.c. *Insoluble in soda*.—Distilling between 100° and 245°, 3 c.c.; 245° and 260°, 120 c.c.; 265° and 285°, 140 c.c.; residue, 50 c.c. The 9 c.c. of oil extracted by light petroleum from the portion soluble in soda was similar to the portion insoluble in soda, and yielded, on distillation between 245° and 265°, 4 c.c.; 265° and 285°, 3 c.c.; residue, 2 c.c.

N. L.

**Constitution of the Campholenic Acids and their Derivatives.** By LOUIS BOUVEAULT (Bull. Soc. Chim., 1898, [iii], 19, 565—573).—The author discusses minutely the reactions, and more especially the behaviour

on oxidation, of  $\alpha$ -campholenic acid,  $\text{CH}_2 \begin{array}{l} \text{CMe}_2 \cdot \text{C} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH} \cdot \text{CH}_2 \cdot \text{COOH} \end{array}$ ;

$\beta$ -campholenic acid,  $\text{CH}_2 \begin{array}{l} \text{CMe}_2 \cdot \text{CMe} \\ \text{CH}_2 - \text{C} \cdot \text{CH}_2 \cdot \text{COOH} \end{array}$ , and the isomeric

lactone,  $\text{CH}_2 \begin{array}{l} \text{CMe}_2 \cdot \text{CMe} \cdot \text{O} \cdot \text{CO} \\ \text{CH}_2 - \text{CH} - \text{CH}_2 \end{array}$ , with a view to showing that the known facts are in full accordance with these formulæ for the compounds.

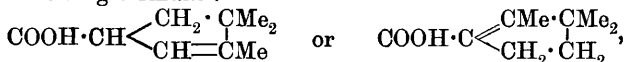
N. L.

**Constitution of Camphoric Acid and Camphor.** By LOUIS BOUVEAULT (Bull. Soc. Chim., 1898, 19, [iii], 462—469).—A theoretical paper discussing the bearing of recent researches on the author's formula for camphoric acid and on the constitution of camphor.

G. T. M.

**Constitution of Isolauronic Acid and Camphoric Acid.** By G. BLANC (Bull. Soc. Chim., 1898, 19, [iii], 533—537. Compare Abstr., 1897, i, 538, 554; this vol., i, 443).—The acid  $\text{C}_8\text{H}_4\text{O}_3$ , obtained by oxidising isolauronic acid with chromic acid mixture, yields  $\alpha\alpha$ -dimethylglutaric acid on treatment with sodium hypobromite, and

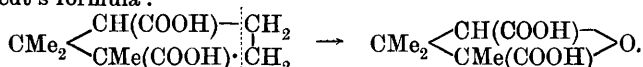
is identical with 3-dimethylhexan-2-onoic acid ( $\gamma$ -acetyldimethylbutyric acid),  $\text{CMe}_2\text{Ac}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , prepared by Tiemann (Abstr., 1897, i, 200). Isolaunonic acid should accordingly be represented by one of the following formulæ :



and since it is optically inactive, the latter is more probable. In accordance with this view, camphoric acid should have the constitution indicated by  $\text{CH}_2\begin{array}{l} \diagup \text{CMe}_2\cdot\text{CMe}\cdot\text{COOH} \\ \diagdown \text{CH}_2-\text{CH}\cdot\text{COOH} \end{array}$ , which is identical with that deduced by Bouveault (compare Perkin, Trans., 1898, 71, 796).

G. T. M.

**Constitution of Camphoric Acid.** By LUIGI BALBIANO (*Ber.*, 1899, 32, 1017—1023. Compare Abstr., 1897, i, 626).—The oxidation of camphoric acid by means of cold alkaline potassium permanganate to the acid  $\text{C}_8\text{H}_{12}\text{O}_5$  and oxalic acid is most readily explained by means of Bredt's formula :



If the Perkin-Bouveault formula (this vol., i, 300) be used, it is necessary to assume the intermediate formation of trimethylglutaric acid; the author now shows that this acid does not appear among the oxidation products, and that it is not oxidised by alkaline permanganate to the acid  $\text{C}_8\text{H}_{12}\text{O}_5$ ; the only oxidation product appears to be a little dimethylsuccinic acid, and the greater part of the acid is not attacked. Perkin's formula does not allow of the formation of the acid  $\text{C}_8\text{H}_{12}\text{O}_5$ .

The acid obtained by oxidation is inactive; it gives a *strychnine* salt which melts at 205—206° when recrystallised eight times from alcohol. When decomposed with alkali, a *dextrorotatory* acid is obtained which melts at 119°, and has  $[\alpha]_D = +5.48^\circ$ , whilst the mother liquors gave a *levorotatory* fraction melting at 117—119°, and having  $[\alpha]_D = -3.35^\circ$ . The formation of a racemic mixture is regarded by the author as evidence in favour of Bredt's formula for camphoric acid, since this represents both asymmetric carbon atoms as being attacked in the oxidation.

T. M. L.

**Crystalline Constituents of Galanga Root.** By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Ber.*, 1899, 32, 861—863).—The crystalline constituents of Galanga root have been investigated by Jahns (Abstr., 1882, 208, 866), who isolated three compounds which were termed campheride, galangin, and alpinin. The first named substance, which has the empirical formula  $\text{C}_{16}\text{H}_{12}\text{O}_6$ , crystallises from methylic alcohol in lustrous, golden needles a centimetre in length; it contains 1 mol. of the solvent, which is removed at 100°, and melts at 227—229°. The *triacetyl* derivative crystallises from alcohol in pale yellow needles, and melts at 193—195°. When the substance is heated with methylic alcohol, potassium hydroxide, and methylic iodide, the *dimethoxymethyl* derivative is produced, along with two compounds melting at 154—155° and 138—140° respectively;

the dimethoxymethyl derivative crystallises from methylic alcohol in rectangular plates and melts at  $178^{\circ}$ . M. O. F.

**Aloin.** By O. A. OESTERLE (*Arch. Pharm.*, 1899, 237, 81—92).—Aloin was dissolved in 96 per cent. alcohol, strong hydrochloric acid added, and the mixture heated in a reflux apparatus for 18—24 hours on the water-bath, and then set aside for days, or even weeks. The brownish deposit was extracted with toluene, the solution boiled with animal charcoal, and the dissolved substance crystallised alternately from toluene and acetic acid. It melts at  $224^{\circ}$ , is orange in colour, has the composition  $C_{15}H_{10}O_5$ , and appears to be identical with the aloë-emodin prepared from Barbados aloes (Tschirch and Pedersen, *Abstr.*, 1898, i, 599), which, when purified as just described, melts at  $223$ — $224^{\circ}$ . Both substances give the same absorption spectra, and both yield yellow *diacetyl* derivatives, melting at  $177$ — $178^{\circ}$  and  $175.5^{\circ}$  respectively.

Aloin was then oxidised by adding it gradually to a mixture of potassium dichromate, water, and strong sulphuric acid heated at  $80$ — $90^{\circ}$  (Tilden, *this Journal*, 1877, ii, 266); in the precipitate that formed, aloxanthin could not be found. By extracting it partially with boiling chloroform, however, finishing the extraction with toluene, and crystallising the extracted substance alternately from toluene and acetic acid, an orange-coloured substance, *alochrysin*, was obtained; this melts at  $223$ — $224^{\circ}$ , and has the composition  $C_{15}H_8O_5$ . Its absorption spectrum, which is described in detail, resembles that of aloxanthin; a yellowish *acetyl* derivative melting at  $245^{\circ}$  was prepared, but not analysed. C. F. B.

**Absinthin.** By PAUL BOURCET (*Bull. Soc. Chim.*, 1898, 19, [iii], 537—539. Compare *Abstr.*, 1892, 1240). The method of separating absinthin from the leaves of *Artemisia absinthium* is fully described. When pure, this glucoside crystallises from dilute alcohol in prismatic needles, melts at  $68^{\circ}$ , and has an extremely bitter taste. Senger's formula for absinthin,  $C_{15}H_{20}O_4$  (*loc. cit.*), is confirmed. G. T. M.

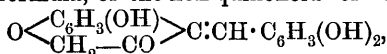
**Brazilin.** By W. FEUERSTEIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1899, 32, 1024—1030).—The dimethylic ether of the oxidation product of brazilin,  $C_9H_6O_4$ , described by Schall and Dralle as crystallising in lustrous, yellow plates which turned white when heated with dilute nitric acid (*Abstr.*, 1892, 502), can be obtained as a colourless, crystalline solid by boiling its alcoholic solution with animal charcoal; on treatment with an alcoholic solution of sodium ethoxide, it gives a mixture of fisetol dimethylic ether,  $OH \cdot C_6H_3(OMe) \cdot CO \cdot CH_2 \cdot OMe$  [= 4 : 2 : 1], and formic acid, the former compound being identical with the substance obtained by Herzig (*Abstr.*, 1891, i, 138) from methyl-fisetin and alcoholic potassium hydroxide, the melting points of the ethylic ether,  $67$ — $68^{\circ}$  (Herzig,  $60$ — $62^{\circ}$ ), and the phenylhydrazone,  $60$ — $61^{\circ}$  (Herzig  $55$ — $57^{\circ}$ ) being only slightly different. It is probable, therefore, that this oxidation product is a 3-hydroxypheno- $\gamma$ -pyronol

$OH \cdot C_6H_3 \begin{matrix} \diagup CO \cdot C \cdot OH \\ \diagdown O - CH \end{matrix}$ ; and bearing in mind that Herzig obtained protocatechuic acid on fusing brazilin with potassium hydroxide, the

following modification of Schall and Dralle's formula for brazilin

is the most probable, 
$$\text{O} \begin{array}{c} \text{C}_6\text{H}_3(\text{OH})^* \\ \text{CH}:\text{C}(\text{OH}) \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2.$$

Brazilein, which is formed from brazilin by the elimination of 2 atoms of hydrogen, can then either have the paraquinonoid structure which would be formed by the elimination of the two hydrogen atoms marked (\*) in the above formula, or the non-quinonoid formula,



and since there are already orange dyes known (Abstr., 1896, i, 606) containing the chromophor  $\text{CO} \cdot \text{C}:\text{C}$ , and it has been shown that the nearer the auxochrome is to the chromophore the more intense the colour, and further that the acidic methylene group,  $\text{CH}_2$ , can act as an auxochrome, it is not at all unlikely that the acidic methylene group in this formula for brazilein acting as the auxochrome is sufficient to change the colour from orange to red. J. F. T.

**Constitution of Brazilin.** By CARL SCHALL (*Ber.*, 1899, 32, 1045—1046).—The formula suggested by Feuerstein and von Kostanekci (compare preceding abstract) is, in the author's opinion, the correct one. J. F. T.

**NOTE.**—This formula is very similar to that recently proposed by Gilbody and Perkin (*Proc.*, 1899, 75), in which the protochatechuic nucleus is attached to the  $\gamma$ -pyrone ring in the ortho-position relatively to the pyrone oxygen. J. F. T.

**Pyrrolidine.** By JULIUS SCHLINCK (*Ber.*, 1899, 32, 947—958. Compare Ciamician and Magnaghi, *Abstr.*, 1885, 1243; Ladenburg, *ibid.*, 1886, 528; 1887, 1052; Gabriel, *ibid.*, 1892, 131).—Various attempts have been made to obtain good yields of pyrrolidine by different methods, but without success.

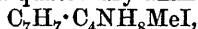
$\gamma$ -Methoxybutyronitrile,  $\text{OMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CN}$ , obtained by the action of methylic alcohol and potassium cyanide on methoxychloropropane (Perkin, *Trans.*, 1894, 65, 596), is an oily liquid which distills at  $172$ — $175^\circ$ , and when reduced with sodium and methylic alcohol yields  $\delta$ -methoxybutylamine; this, when dried over solid potassium hydroxide, forms a clear liquid boiling at  $142$ — $145^\circ$  and having a strongly alkaline reaction; the hydrochloride is extremely hygroscopic and readily soluble in alcohol, and the platinochloride,  $(\text{C}_5\text{H}_{13}\text{NO})_2 \cdot \text{H}_2\text{PtCl}_6$ , crystallises in glistening, golden plates decomposing at  $175^\circ$  without melting. The base combines with phenylthiocarbamide, yielding phenyl- $\delta$ -methoxybutylthiocarbamide,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_4\text{H}_8 \cdot \text{OMe}$ , which crystallises from water in glistening plates or prisms melting at  $70.5^\circ$ . As the yield of methoxybutylamine is little or no better than that of the phenoxy-compound (Gabriel, *loc. cit.*), no attempt was made to convert it into pyrrolidine.

When sodium paratolyloxide is boiled for  $1\frac{1}{2}$  hours with an alcoholic solution of chlorobutyronitrile, it yields  $\gamma$ -paratolyloxybutyronitrile,  $\text{C}_7\text{H}_7\text{O} \cdot \text{C}_3\text{H}_6 \cdot \text{CN}$ , a yellowish oil distilling at  $296$ — $298^\circ$  and solidifying in small plates melting at  $17$ — $18^\circ$ ; when hydrolysed with concentrated

hydrochloric acid, the nitrile yields *paratolylxybutyric acid*, which crystallises from light petroleum in glistening plates melting at  $87^{\circ}$ , and when reduced with sodium and alcohol is converted into  $\delta$ -*paratolylxybutylamine*, which is a colourless oil with a disagreeable odour and boils at  $262-271^{\circ}$ . The *hydrochloride* of this base crystallises in needles, the *platinochloride*,  $(C_{11}H_{17}NO)_2 \cdot H_2PtCl_6$ , in large, yellow, rhombic prisms melting and decomposing at  $216^{\circ}$ , the *aurichloride*,  $C_{11}H_{17}NO \cdot HAuCl_4$ , in golden-yellow plates and prisms decomposing at  $73^{\circ}$ ; the *dichromate*,  $(C_{11}H_{18}NO)_2 \cdot Cr_2O_7$ , begins to melt at  $80^{\circ}$  and is completely decomposed at  $122^{\circ}$ ; the *picrate* forms long, yellow needles melting at  $151-152^{\circ}$ . The base combines with phenylthiocarbimide, yielding *phenyl paratolylxybutylthiocarbamide*, which crystallises from alcohol in indented needles melting at  $107.5-109^{\circ}$ ; when heated for 10 hours at  $100^{\circ}$  with concentrated hydrochloric acid, the base is converted into  $\delta$ -chlorobutylamine, and this may then be converted into pyrrolidine, but the yield is practically the same as by Gabriel's method.

The reduction of succinimide by the aid of amylic alcohol and sodium in place of ethylic alcohol (Ladenburg) leads to the formation of only minute traces of pyrrolidine; the reduction of pyrrolidone (Gabriel, Abstr., 1890, 360) and of pyrroline do not give any better yield.

1-*Benzylpyrrolidine*,  $C_4NH_8 \cdot C_7H_7$ , is readily obtained by the action of benzylic chloride on pyrrolidine as a clear, oily liquid of faint, disagreeable odour boiling at  $237^{\circ}$ , its *hydrochloride* crystallises from a strongly acid solution in large, rhombic, deliquescent plates; the *platinochloride* forms yellowish-red needles melting and decomposing at  $156^{\circ}$ , the *aurichloride* crystallises in lemon-yellow needles melting and decomposing at  $120^{\circ}$ , the *picrate* is readily soluble in water or alcohol, and melts at  $128^{\circ}$ . The base itself readily combines with methylic iodide, forming a quaternary ammonium compound,



which is readily soluble in acids, water, or alcohol; the *picrate* melting at  $119^{\circ}$ , the *platinochloride*,  $(C_{12}H_{17}N)_2 \cdot H_2PtCl_6$ , melting at  $183-184^{\circ}$ , and the *aurichloride* melting at  $90.5^{\circ}$ , have been prepared.

*Paranitrobenzylpyrrolidine*, obtained by the action of paranitrobenzylic chloride on an alcoholic solution of pyrrolidine at  $100^{\circ}$ , is a somewhat pleasant smelling oil which cannot be distilled without undergoing decomposition; the *picrate* crystallises in slender, lemon-yellow needles melting at  $151-153^{\circ}$ , the *platinochloride* melts and decomposes at  $160^{\circ}$ , and the *aurichloride* at  $155^{\circ}$ . *Orthonitrobenzylpyrrolidine* also forms a yellowish oil which undergoes decomposition when distilled; its *aurichloride* crystallises in slender, golden-yellow prisms melting and decomposing at  $160^{\circ}$ , and readily soluble in ether but sparingly so in water; its *picrate* melts at  $152.5^{\circ}$ .

Pyrrolidine reacts with both aliphatic and aromatic thiocarbimides, yielding well defined crystalline derivatives, of which the following have been examined: *Pyrrolidinephenylthiocarbamide*,



crystallises from hot water in needles or rhombic plates melting at

148.5°. *Pyrrolidinemethylthiocarbamide* forms long needles melting at 117°; the *ethyl* compound melts at 91°, the *allyl* compound sinters and then melts at 70°.

*Pyrrolidineallyl-ψ-thiocarbamide*,  $\begin{array}{c} \text{CHMe} \cdot \text{S} \\ | \\ \text{CH}_2 - \text{N} \end{array} \begin{array}{c} \text{S} \\ \text{C} \cdot \text{N} \end{array} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$  (compare Gabriel, Abstr., 1889, 848; 1890, 127), formed when pyrrolidineallylthiocarbamide is heated with fuming hydrochloric acid for 2 hours at 100°, is a yellowish oil sparingly soluble in water which yields an *aurichloride* melting at 107–108° and a *platinochloride* melting and decomposing between 182° and 201°.

1-γ-Phenoxypropylpyrrolidine,  $\text{OPh} \cdot \text{C}_3\text{H}_6 \cdot \text{C}_4\text{NH}_8$ , obtained by the action of pyrrolidine on γ-phenoxypropylic chloride, is a brownish oil which boils at 288.5° and yields a *platinochloride* melting and decomposing at 160–161°. When treated according to Gabriel and Stelzner's method (Abstr., 1896, i, 703), it yields γ-bromopropylpyrrolidine hydrobromide,  $\text{C}_4\text{NH}_8 \cdot \text{C}_3\text{H}_6\text{Br} \cdot \text{HBr}$ , as an extremely hygroscopic solid; the *picrate* sinters at 119° and melts at 123°. Attempts to obtain trimethylene pyrrolylium bromide proved unsuccessful.

J. J. S.

**Action of αδ-Dibromopentane on Primary and Secondary Bases.** By MAX SCHOLTZ and P. FRIEMEHLT (*Ber.*, 1899, 32, 848–853).—The action of 1:4-dibromopentane on bases is less energetic than that of orthoxylylenic bromide (compare Abstr., 1898, i, 565), but follows the same lines.

1:2-Phenylmethylpyrrolidine,  $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{NPh}$ , prepared by heating an alcoholic solution of αδ-dibromopentane with excess of aniline, is a colourless liquid boiling at 134° under 25 mm. pressure; the *platinochloride* crystallises in needles, and the *picrate* melts at 105°.

αδ-Diorthotoluidinopentane,

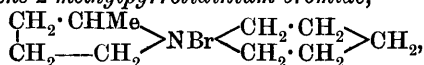
$\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , prepared by heating αδ-dibromopentane with orthotoluidine, boils at 191–193° under 23 mm. pressure; the *picrate* crystallises from alcohol in needles and melts at 147°.

1:2-Paratolylmethylpyrrolidine,  $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{N} \cdot \text{C}_6\text{H}_4\text{Me}$ , formed when paratoluidine acts on αδ-dibromopentane, is a colourless oil which boils at 147–149° under 20 mm. pressure; the *picrate* crystallises from dilute alcohol in microscopic needles and melts at 117°.

1-Metanitrophenyl-2-methylpyrrolidine,  $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , obtained from αδ-dibromopentane and metanitriline, crystallises in brownish-red needles on adding petroleum to the benzene solution and melts at 140°.

αδ-Diorthonitranilinopentane,  $\text{C}_5\text{H}_{10}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , crystallises in orange-red needles and melts at 172°.

Pentamethylene-2-methylpyrrolidinium bromide,



prepared by the action of alcoholic piperidine on  $\alpha\delta$ -dibromopentane, is a crystalline, hygroscopic salt; the *platinochloride* and *aurichloride* melt at  $250^\circ$  and  $220^\circ$  respectively. M. O. F.

**Perbromides of some Cyclic Acetone Bases.** By A. SAMTLEBEN (*Ber.*, 1899, 32, 663—667).—When 4-hydroxy-1:2:2:6:6-pentamethylpiperidine hydrobromide perbromide (Abstr., 1898, i, 473, where 4-hydroxy is inadvertently omitted), is digested with aqueous sodium carbonate, hydroxypentamethylpiperidine is regenerated for the most part, but a little 1-bromo-4-hydroxy-2:2:6:6-tetramethylpiperidine is formed; this is interesting, as it exemplifies the formation of a secondary from a tertiary amine.

4-Bromo-2:2:6:6-tetramethylpiperidine is obtained by heating hydroxytetramethylpiperidine with four times its weight of fuming hydrobromic acid for an hour at  $150^\circ$ ; it melts at  $45^\circ$ , and in the air undergoes a slow transformation into the hydrobromide of 2:2:6:6-tetramethyl- $\Delta_3$ -tetrahydropyridine (triacetone); its *hydrobromide* forms an orange-yellow *perbromide*,  $C_9NH_{13}Br \cdot Br_2$ , when dissolved in cold, dilute hydrobromic acid and treated with bromine; this loses its bromine readily, and when it is stirred with dilute aqueous sodium carbonate forms yellow 1:4-dibromo-2:2:6:6-tetramethylpiperidine, which melts at  $45^\circ$ .

4-Iodo-2:2:6:6-tetramethylpiperidine, which can be obtained from the 4-hydroxy-compound and hydriodic acid at  $150^\circ$ , forms an orange-yellow hydrobromide perbromide, and by the action of sodium carbonate on this, 1-bromo-4-iodo-2:2:6:6-tetramethylpiperidine is obtained; it melts at  $98^\circ$ , and loses its bromine when boiled with acids, but not with alkalis or water.

2:2:6:6-Tetramethyl- $\Delta_3$ -tetrahydropyridine hydrobromide yields an orange-red *perbromide* when treated with bromine at the ordinary temperature; this melts at about  $55^\circ$ , and at a higher temperature undergoes a molecular transformation into 3:4-dibromo-2:2:6:6-tetramethylpiperidine, which decomposes at  $170^\circ$ ; the base corresponding with this could not be isolated, as alkalis remove all the bromine, regenerating  $\Delta_3$ -tetrahydropyridine. C. F. B.

**Stereochemistry of Quinquevalent Nitrogen. Quadrivalent Sulphur.** By OSSIAN ASCHAN (*Ber.*, 1899, 32, 988—994. Compare Wedekind, this vol., i, 351, and Marckwald and Droste-Huelshoff, *ibid.*, 326).—*Diethylenedipiperidyl iodide*,  $C_5H_{10}NI \cdot (C_2H_4)_2 \cdot NC_5H_{10}I$ , crystallises from water in brownish, glistening flakes, and melts at  $295^\circ$ ; like the bromide, it is only known in one form. *Propylenedipiperidide*,  $C_5H_{10}N \cdot CHMe \cdot CH_2 \cdot C_5H_{10}N$ , boils at  $265$ — $266^\circ$ , and, when combined with ethylenic dibromide, gives an *ethylenepropylenedipiperidyl bromide* different from that which is obtained by the inter-action of ethylene dipiperidide and propylenic bromide.

*Ethylenedipiperidyl dimethiodide* exists in two triclinic modifications [ $a:b:c = 1.887:1:0.429$ ,  $\alpha = 88^\circ 42'$ ,  $\beta = 88^\circ 55\frac{1}{2}'$ ,  $\gamma = 100^\circ 45'$ ;  $a:b:c = 1.012:1:0.809$ ,  $\alpha = 80^\circ 22\frac{1}{2}'$ ,  $\beta = 79^\circ 49'$ ,  $\gamma = 95^\circ 41'$ ], of which the latter has the higher melting point by  $3^\circ$ . These are both produced by the action of methylic iodide on ethylenedipiperidide, together



with a little of the *monomethiodide* melting at  $155.5^{\circ}$ , and are regarded as analogous to racemic and mesotartaric acids.

The additive compounds of methylenic and ethylenic iodides and ethylenic bromide with methylic ethylic sulphide have also been prepared, in order to establish, if possible, the existence of racemic and meso-forms. T. M. L.

**Action of Alkylid Iodides on Indoles.** 2':3':3'-Trimethylindolenine. By GIUSEPPE PLANCHER and D. BETTINELLI (*Gazzetta*, 1899, 29, i, 106—120. Compare Abstr., 1898, i, 536).—In preparing 2':3':3'-trimethylindolenine by the condensation of methyl isopropyl ketone with phenylhydrazine in presence of zinc chloride, the latter forms, with the base, a double compound, which the authors have now shown to have the composition  $\text{ZnCl}_2(\text{C}_{11}\text{H}_{13}\text{N})_2$ . The free trimethylindolenine produces in benzene solution the normal depression of freezing point. A small quantity of an indole formed in the above condensation proves to be 2':3'-dimethylindole.

2':3':3'-Trimethylindolenine forms a *benzoyl* derivative,  $\text{C}_{11}\text{H}_{13}\text{NBz}$ , which crystallises from alcohol in white needles melting unchanged at  $183^{\circ}$ , is almost insoluble in benzene or light petroleum, has the normal molecular weight in bromoform solution, is stable towards permanganate, and is readily hydrolysed by acids or alkalis.

3':3'-Dimethylindolenine-2'-formoxime,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{CMe}_2 \end{array} \text{C} \cdot \text{CH} \cdot \text{NOH}$ , prepared by acting on an acetic acid solution of the trimethylindolenine with cold potassium nitrite solution, crystallises from a mixture of benzene and light petroleum in white needles or prisms melting at  $156^{\circ}$ . It is soluble in caustic alkalis, and is reprecipitated by carbonic anhydride. On heating with excess of acetic anhydride, it gives rise to 3':3'-dimethylindolenine-2'-formonitrile,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{CMe}_2 \end{array} \text{C} \cdot \text{CN}$ , which is a colourless oil having a pleasant smell, boils at  $150\text{--}151^{\circ}$  under 30 mm. pressure, and is soluble in the ordinary organic solvents. When heated with hydrochloric acid, this nitrile yields the 3':3'-dimethylindolinone obtained by Brunner (Abstr., 1897, i, 438); this crystallises from ethylic acetate in orthorhombic crystals [ $a:b:c = 0.8521:1:0.7212$ ]. Brunner's compound gave [ $a:b:c = 0.8496:1:0.7219$ ].

When trimethylindolenine is oxidised with permanganate, it yields a small quantity of an acid melting at  $140^{\circ}$ , the constitution of which was not determined. On reduction with tin and hydrochloric acid, the secondary trimethylindoline prepared by Ferratini (Abstr., 1894, i, 96) is obtained. T. H. P.

**Action of Alkalis on Orthomethyldiazonium Salts.** By EUGEN BAMBERGER (*Annalen*, 1899, 305, 289—370).—It has been shown that, under certain conditions (Abstr., 1896, i, 300), alkalis convert diazonium salts into the highly explosive diazo-anhydrides, in accordance with the equation  $2\text{Arr} \cdot \text{N}_2 \cdot \text{Cl} + 2\text{NaOH} = 2\text{NaCl} + \text{H}_2\text{O} + (\text{Arr} \cdot \text{N}_2)_2\text{O}$  [Arr. is an abbreviation of arryl, which term the author now employs to express univalent aromatic radicles]; the action is

not general, however, and does not apply to 2:4:6-tribromodiazobenzene, which yields 3:5-dibromo-2-diazo-1-phenol,  $C_6H_2Br_2\langle\begin{smallmatrix} O \\ N \end{smallmatrix}\rangle N$ .

Orthodiazotoluene gives rise to indazole,  $C_6H_4\langle\begin{smallmatrix} CH \\ N \end{smallmatrix}\rangle NH$ , described by Fischer and Tafel, whilst diazomesidine yields 1:3-dimethylindazole, along with an orange-yellow compound having the empirical formula  $C_{18}H_{20}N_4$ , and probably representing the mesitylazo-derivative of the dimethylindazole; the bye-products which accompany the formation of these two substances are mesitol, mesitylene, chloromesitylene, mesidine, and mesitylenic acid.

1:3-Dimethylindazole,  $C_6H_2Me_2\langle\begin{smallmatrix} CH \\ N \end{smallmatrix}\rangle NH$ , prepared from diazomesidine and caustic soda under conditions described in the original paper, crystallises from a mixture of benzene and petroleum in slender, white needles melting at  $133-134^\circ$ ; the acetyl derivative crystallises from alcohol in white needles, and melts at  $116-117^\circ$ .

3'-Mesitylazo-1:3-dimethylindazole,  $C_6H_2Me_2\langle\begin{smallmatrix} C(N_2 \cdot C_6H_2Me_3) \\ N \end{smallmatrix}\rangle NH$ , crystallises from alcohol or glacial acetic acid in lustrous, orange-yellow needles melting at  $258^\circ$ , and subliming in very slender, sulphur-yellow needles; the solution in concentrated sulphuric acid is bluish-violet, becoming cherry-red when treated with a nitrate or a nitrite. The substance is formed, not only in the manner described above, but also by the action of diazotised mesidine on dimethylindazole. Reduction with stannous chloride, or with alcoholic ammonium sulphide, resolves the azo-compound into mesidine and

3'-amido-1:3-dimethylindazole,  $C_6H_2Me_2\langle\begin{smallmatrix} C(NH_2) \\ N \end{smallmatrix}\rangle NH$ , which crystallises from a mixture of benzene and petroleum in slender, white needles and melts at  $150-151^\circ$ ; this base dissolves somewhat readily in water, the solution giving characteristic precipitates with solutions of metallic salts, and developing a reddish-violet coloration when agitated with sodium hydroxide. Mesitylazodimethylindazole yields dimethylindazole, mesidine, and ammonia when reduced with sodium in ethylic alcohol.

3'-Benzeneazo-1:3-dimethylindazole,  $C_6H_2Me_2\langle\begin{smallmatrix} C(N_2Ph) \\ N \end{smallmatrix}\rangle NH$ , prepared by the action of diazotised aniline on dimethylindazole, crystallises from benzene in concentric aggregates of golden-yellow needles, and melts at  $206.5-207.5^\circ$ .

The benzylidene derivative of 3'-amido-1:3-dimethylindazole crystallises from benzene or alcohol in colourless needles and melts at  $183.5-184.5^\circ$ ; the thiocarbamide derivative,  $C_6H_2Me_2\langle\begin{smallmatrix} C-NH \\ N \end{smallmatrix}\rangle CS$ , crystallises from petroleum in slender, pale yellow needles, and melts at  $208-209^\circ$ . The benzenesulphonamide crystallises from dilute alcohol in lustrous, rectangular leaflets and melts at  $232-233^\circ$ . The diazo-

*hydroxide*, prepared by diazotising the base in presence of the minimum quantity of mineral acid, decomposes at  $130^{\circ}$ , and dissolves sparingly in water, forming dimethylindazoletriazoline; the solution in hydrochloric acid contains dimethylindazoletriazoline hydrochloride, whilst the alkaline solutions consist of normal alkali dimethylindazoleindates.

*Dimethylindazoleazo- $\beta$ -naphthol*,  $\text{C}_6\text{H}_2\text{Me}_2 \left\langle \underset{\text{N}}{\overset{\text{C}(\text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH})}{|}} \right\rangle \text{NH}$ ,

prepared from diazotised amidodimethylindazole and the naphthol, crystallises from xylene in bronze-coloured needles with greenish-gold reflex; it melts at  $266\text{--}267^{\circ}$  when quickly heated, and forms an indigo-blue solution in sulphuric acid, changing to magenta-red when treated with a crystal of nitre.

*3-Chloro-1:3-dimethylindazole*,  $\text{C}_6\text{H}_2\text{Me}_2 \left\langle \underset{\text{N}}{\overset{\text{CCl}}{|}} \right\rangle \text{NH}$ , prepared by heating amidodimethylindazole diazohydroxide with concentrated hydrochloric acid in a reflux apparatus, sublimes in slender needles and melts at  $174^{\circ}$ .

*1:3-Dimethyl-4'-hydroxy- $\beta$ -phenotriazine*,  $\text{C}_6\text{H}_2\text{Me}_2 \left\langle \underset{\text{N}=\text{N}}{\overset{\text{C}(\text{OH})}{|}} \right\rangle \text{N}$ , obtained by oxidising amidodimethylindazole with hydrogen peroxide, crystallises from benzene in aggregates of slender, lustrous needles and melts at  $219\text{--}220^{\circ}$ , yielding gas.

[With ANTON VON GOLDBERGER.]—*3'-Orthotolueneazoindazole*,  $\text{C}_6\text{H}_4 \left\langle \underset{\text{N}}{\overset{\text{C}(\text{N}_2 \cdot \text{C}_6\text{H}_4\text{Me})}{|}} \right\rangle \text{NH}$ , a bye-product in the formation of indazole on treating diazotised orthotoluidine with sodium hydroxide, is also obtained by combining indazole with diazotoluidine; it crystallises from boiling xylene in slender, orange-yellow needles and melts at  $211\text{--}211.5^{\circ}$ .

*3'-Benzeneazoindazole*,  $\text{C}_6\text{H}_4 \left\langle \underset{\text{N}}{\overset{\text{C}(\text{N}_2\text{Ph})}{|}} \right\rangle \text{NH}$ , prepared from diazonium chloride and indazole, also crystallises from xylene in orange-yellow needles, and melts at  $185.5\text{--}186^{\circ}$ .

*3'-Amidoindazole*,  $\text{C}_6\text{H}_4 \left\langle \underset{\text{N}}{\overset{\text{C}(\text{NH}_2)}{|}} \right\rangle \text{NH}$ , obtained by reducing the foregoing azo-compound with ammonium sulphide, crystallises slowly from a mixture of ether and benzene in beautiful, highly lustrous, monoclinic prisms melting at  $153.5\text{--}154.5^{\circ}$ ; an intense red coloration is developed when sodium hydroxide is added to the aqueous solution exposed to air or in presence of potassium ferricyanide. Characteristic results are obtained on treating the aqueous solution of amidoindazole with Fehling's solution, and with solutions of silver nitrate, bleaching powder, ferric chloride, and chromic acid. The *sulphate* crystallises in needles, and melts at  $223\text{--}224^{\circ}$ ; the *oxalate*, *picrate*, and *hydrochloride* are also crystalline. The *diacetyl* derivative crystallises from dilute alcohol in silky, white needles and melts at  $177\text{--}178^{\circ}$ ; the *dibenzoyl* derivative separates from xylene in lustrous, transparent needles and melts at  $182^{\circ}$ . The *paranitrobenzylidene* derivative melts

at 232—234°. When amidindazole is reduced in alcoholic solution with sodium, indazole is formed.

*Diazoindazole hydroxide*,  $C_6H_4 \left\langle \begin{smallmatrix} C(N:N\cdot OH) \\ N \end{smallmatrix} \right\rangle NH$ , precipitated when a 10 per cent. solution of sodium nitrite is added to amidindazole dissolved in 2 per cent. hydrochloric acid, decomposes at 128°. It closely resembles the dimethylic derivative in chemical behaviour, and yields indazoletriazoline when treated with boiling water during a few minutes; protracted action, however, converts it into a crystalline substance which is volatile in steam and soluble in aqueous sodium hydroxide, probably consisting of the corresponding phenol.

*Indazoleazo- $\beta$ -naphthol*,  $C_6H_4 \left\langle \begin{smallmatrix} C(N_2 \cdot C_{10}H_6 \cdot OH) \\ N \end{smallmatrix} \right\rangle NH$ , prepared from diazoindazole hydroxide and  $\beta$ -naphthol, crystallises from amyl alcohol or from xylene in slender, deep red needles, and melts at 250—251°.

*Diazoamidindazole*,  $C_7H_5N_2 \cdot N:N \cdot NH \cdot C_7H_5N_2$ , obtained on adding diazotised amidindazole to a solution of the base in hydrochloric acid, forms a dark yellow, amorphous powder, and decomposes at 183°; aqueous sodium hydroxide develops a green coloration, which becomes red, and then brown, an odour of nitrobenzene being ultimately produced.

*3'-Chlorindazole*,  $C_6H_4 \left\langle \begin{smallmatrix} CCl \\ N \end{smallmatrix} \right\rangle NH$ , prepared from amidindazole by the Sandmeyer reaction, crystallises from water or from petroleum in very long, silky needles, and melts at 148—148.5°; it is acidic in character, being soluble in cold, dilute aqueous sodium hydroxide. Mercuric chloride and silver nitrate yield sparingly soluble double salts, and bromine water produces a white, crystalline precipitate in very dilute solutions.

*4'-Hydroxy- $\beta$ -phenotriazine*,  $C_6H_2Me_2 \left\langle \begin{smallmatrix} C(OH) \\ N=N \end{smallmatrix} \right\rangle N$ , obtained on oxidising amidindazole with hydrogen peroxide, crystallises from water or from benzene in snow-white, lustrous needles and melts at 213°; it is identical with benzazimide, described by Weddige and Finger (Abstr., 1887, 667). Hydroxyphenotriazine is also formed by the action of ammonia on ethylic anthranilate (compare Zacharias, Abstr., 1891, 912).

*3-Methylindazole*,  $C_6H_3Me \left\langle \begin{smallmatrix} CH \\ N \end{smallmatrix} \right\rangle NH$ , prepared by the action of sodium hydroxide on diazotised unsymmetrical metaxylydine, is identical with Gabriel and Stelzner's 3-methylindazole (Abstr., 1896, i, 320); it crystallises from water or from petroleum in white needles and melts at 114—115°.

*3'-Metaxyleneparazo-3-methylindazole*,  $C_6H_3Me \left\langle \begin{smallmatrix} C(N_2 \cdot C_6H_3Me_2) \\ N \end{smallmatrix} \right\rangle NH$ , formed as a bye-product in the preparation of 3-methylindazole, crystallises in yellow nodules, and sublimes in bright yellow, slender needles; it melts at 228—229° and dissolves in concentrated sulphuric

acid, forming an intense violet coloration, which becomes orange-red on adding a crystal of nitre. Reduction with stannous chloride or ammonium sulphide resolves the azo-compound into 1:3:4-xylydine and 3-methyl-3'-amidoindazole,  $C_6H_3Me \begin{smallmatrix} C(NH_2) \\ \diagup \quad \diagdown \\ N \end{smallmatrix} NH$ , which crystallises from benzene in lustrous, white leaflets and melts at  $190.5-191.5^\circ$ ; when the aqueous solution is agitated with sodium hydroxide in presence of air or potassium ferrieyanide, a violet-red coloration is produced. Characteristic changes are brought about by Fehling's solution and by solutions of mercuric chloride, silver nitrate, picric acid, ferric chloride, and bleaching powder; alkaline permanganate is instantly reduced, and nitrous acid gives rise to the diazo-hydroxide.

3-Methyl-4'-hydroxy- $\beta$ -phenotriazine,  $C_6H_3Me \begin{smallmatrix} C(OH) \\ \diagup \quad \diagdown \\ N=N \end{smallmatrix} N$ , produced on oxidising methylamidindazole with hydrogen peroxide, crystallises in white needles and melts at  $228^\circ$ . M. O. F.

Imidophenyltriazoline. By GEROLAMO CUNEO (*Gazzetta*, 1899, 29, i, 12-32).—Phenylamidoguanidine hydrochloride and sodium formate, when boiled together in formic acid solution, yield a compound

which is either 3-imido-1-phenyltriazoline,  $NPh \begin{smallmatrix} NH \cdot C : NH \\ \diagup \quad \diagdown \\ CH : N \end{smallmatrix}$ , or an amidotriazole derivative,  $NPh \begin{smallmatrix} N=C \cdot NH_2 \\ \diagup \quad \diagdown \\ CH : N \end{smallmatrix}$ . To decide between these

constitutions, it was methylated and acetylated, when it yielded mono- and di-derivatives in both cases; this behaviour agrees with either formula. Attempts to decompose the methyl compounds by the action of acids or alkalis gave negative results. The formation of a benzylidene derivative, although explained better by the amido-formula, does not exclude the imido-constitution, which is favoured by the formation of a nitroso-derivative with nitrous acid.

3-Imido-1-phenyltriazoline crystallises from boiling water in long, colourless, silky needles melting at  $150^\circ$ , and is very soluble in alcohol or ether. Its hydrochloride,  $C_8N_4H_8 \cdot HCl + H_2O$ , is very soluble in water or alcohol, and crystallises from dilute hydrochloric acid solution in long, colourless, monoclinic needles melting at  $187^\circ$  [ $a:b:c = 1.17999:1.060475$ ;  $\beta = 82^\circ 52'$ ]. The nitrate,  $C_8N_4H_8 \cdot HNO_3$ , separates from water in long, thin, colourless needles soluble in alcohol and melting at  $181^\circ$ . The picrate,  $C_8N_4H_8 \cdot C_6H_3N_3O_7$ , forms yellow needles which melt at  $220^\circ$ , and are soluble in water or alcohol. The platinum-chloride,  $(C_8N_4H_8)_2 \cdot H_2PtCl_6 + 2H_2O$ , is slightly soluble in alcohol or ether, and separates from hydrochloric acid solution in long, orange-red plates; when heated or treated with boiling water, it is converted into tetrachloroplatinophenylimidotriazoline,  $(C_8N_4H_8)_2PtCl_4$ , a pale yellow, amorphous, flocculent substance insoluble in water.

2-Nitroso-3-imido-1-phenyltriazoline,  $C_8N_4H_7 \cdot NO$ , obtained by the action of nitrous acid on phenylimidotriazoline, forms yellowish crystals and is very soluble in alcohol.

Benzylideneimidophenyltriazoline,  $C_8N_4H_6 \cdot CHPh$ , forms colourless crystals melting at  $155^\circ$ , and is very soluble in alcohol or chloroform,

less so in ether. On boiling with water or on dissolving in cold hydrochloric acid, an odour of benzaldehyde is produced.

2-Acetyl-3-imido-1-phenyltriazoline,  $C_8N_4H_7Ac$ , obtained by the action of acetic anhydride on imidophenyltriazoline, separates from alcohol in colourless crystals melting at  $168^\circ$ . 2-Acetyl-3-acetimido-1-phenyltriazoline,  $C_8N_4H_6Ac_2$ , forms colourless needles melting at  $118^\circ$  and dissolving readily in alcohol or carbon bisulphide.

3-Imido-1-phenyl-2-methyltriazoline,  $C_8N_4H_7Me$ , prepared by the action of methylic iodide on imidophenyltriazoline, separates as the hydriodide,  $C_8N_4H_7Me.HI + H_2O$ , which crystallises from water in broad, orange-yellow, iridescent plates, and melts at  $170^\circ$ ; the picrate,  $C_8N_4H_7Me.C_6H_3N_3O_7$ , forms orange-red prisms melting at  $184^\circ$ , and dissolves sparingly in water or ether, but readily in alcohol.

3-Methylimido-1-phenyl-2-methyltriazoline,  $C_8N_4H_6Me_2$ , is an oil; its picrate,  $C_8N_4H_6Me_2.C_6H_3N_3O_7$ , crystallises in bright yellow, silky needles melting at  $201^\circ$  with decomposition; it is slightly soluble in ether, more so in water, and very readily in alcohol.

Bromophenylimidotriazoline,  $C_8N_4H_7Br$ , crystallises from alcohol in groups of beautiful, orange-yellow plates melting at  $196^\circ$ ; it dissolves readily in alcohol or chloroform, but only slightly in water or ether.

$\alpha$ -Phenylmethylsemicarbazide,  $NH_2.CO.NMe.NHPh$ , obtained by the action of formic acid on phenylamidomethylguanidine, crystallises from water in large, colourless plates melting at  $147^\circ$ ; it is very soluble in alcohol, ether, chloroform, or boiling water, and insoluble in carbon bisulphide. To confirm its constitution, it was prepared synthetically from cyanic acid and methylphenylhydrazine.

By reducing phenylimidourazole by means of phosphorus pentasulphide, the same imidophenyltriazoline is obtained as results from the reaction of formic acid and phenylamidoguanidine.

T. H. P.

**New Triazoline Compounds.** By GEROLAMO CUNEO (*Gazzetta*, 1899, 29, i, 89—106).—The author finds that reactions analogous to that between formic acid and phenylamidoguanidine take place with other acids, and also with other derivatives of amidoguanidine.

3-Imido-1-paratolyltriazoline,  $C_7H_7.N \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{NH} \\ | \\ \text{CH} : \text{N} \end{smallmatrix}$ , obtained by prolonged boiling of a formic acid solution of equivalent quantities of paratolylamidoguanidine and dry sodium formate, crystallises in beautiful, colourless needles, melts at  $185^\circ$ , and is very soluble in alcohol or chloroform. Its hydrochloride,  $C_7N_4H_{10}.HCl$ , forms beautiful, colourless, monoclinic needles [ $a:b:c = 2.19444:1.475266$ ;  $\beta = 72^\circ 41'$ ], which show signs of fusion at  $225^\circ$  and melt completely and decompose at  $234^\circ$ . It is almost insoluble in ether or chloroform, but dissolves moderately in water, and more so in alcohol. The platinochloride,  $(C_7N_4H_{10})_2.H_2PtCl_6$ , forms small, orange-coloured needles almost insoluble in alcohol or ether; when heated at  $200^\circ$ , it loses  $2HCl$  very quickly, and then goes on gradually decreasing in weight.

3-Imido-1-orthotolyltriazoline,  $C_7H_7.N \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{NH} \\ | \\ \text{CH} : \text{N} \end{smallmatrix}$ , prepared by boiling together, in molecular proportion, orthotolylamidoguanidine

hydrochloride and dry sodium formate in glacial formic acid solution, forms beautiful, colourless, prismatic needles melting at  $122^{\circ}$ . Its *picrate*,  $C_9N_4H_{10} \cdot C_6H_3N_3O_7$ , separates from alcohol in beautiful, yellow, lozenge-shaped crystals melting at  $192^{\circ}$  and moderately soluble in water or alcohol.

3-Imido-1-phenyl-5-methyltriazoline,  $NPh \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{NH} \\ \text{CMe} : \text{N} \end{smallmatrix}$ , produced by

heating a mixture of equivalent proportions of phenylamidoguanidine hydrochloride and dry sodium acetate in presence of an excess of acetic anhydride, is only slightly soluble in ether, but more so in water, alcohol, or chloroform. It crystallises from water in beautiful, colourless, monoclinic prisms melting at  $186^{\circ}$  [ $a : b : c = 1.28824 : 1 : 2.13496$ ;  $\beta = 53^{\circ} 38'$ ]. Its *hydrochloride*,  $C_9H_{10}N_4 \cdot HCl + H_2O$ , crystallises in cubes which are very soluble in water. The *platinochloride*,  $(C_9H_{10}N_4)_2 \cdot H_2PtCl_6$ , crystallises from its hydrochloric acid solution in large, orange-coloured, monoclinic prisms melting and decomposing at  $245^{\circ}$  [ $a : b : c = 3.21435 : 1 : 4.34494$ ;  $\beta = 61^{\circ} 40'$ ].

Dibenzoyl-3-imido-1:5-diphenyltriazoline,  $C_2N_4Ph_2Bz_2$ , obtained by heating phenylamidoguanidine hydrochloride and sodium benzoate, in molecular proportion, with excess of benzoic chloride, separates from alcohol in crystals melting at  $194$ – $195^{\circ}$ , and it is neither acid nor basic in its properties. On hydrolysis, it yields 3-imido-1:5-diphenyltriazoline,

$ine$ ,  $NPh \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{NH} \\ \text{CPh} : \text{N} \end{smallmatrix}$ , which crystallises from alcohol in monoclinic

laminæ melting at  $156^{\circ}$  [ $a : b : c = 0.88175 : 1 : 0.77171$ ;  $\beta = 82^{\circ} 6'$ ]. It dissolves very slightly in water, but is very soluble in alcohol, ether, or chloroform. It has no basic properties, being almost insoluble in dilute mineral acids, and forming neither a *picrate* nor a *platinochloride*. On boiling with an excess of acetic anhydride, it yields a *diacetyl* derivative,  $C_2N_4Ph_2Ac_2$ , which crystallises from light petroleum in stellate groups of lustrous needles melting at  $119^{\circ}$ ; it is soluble in alcohol, chloroform, benzene, or light petroleum, and on boiling with water, acetic acid is evolved and imidodiphenyltriazoline reproduced.

5:5-Phenylene-bis-3-imido-1-phenyltriazoline,  $C_6H_4 \left( C \begin{smallmatrix} \text{NPh} \cdot \text{NH} \\ \text{N} \text{---} \text{C} \cdot \text{NH} \end{smallmatrix} \right)_2$ , is formed on heating corresponding quantities of phenylamidoguanidine hydrochloride and potassium phthalate with an excess of phthalic chloride; it crystallises from alcohol in acicular plates melting at  $261^{\circ}$ , is almost insoluble in water or ether, but dissolves in alcohol or chloroform, and has basic properties, as it dissolves readily in mineral acids and is reprecipitated by potash.

5:5-Ethylene-bis-3-imido-1-phenyltriazoline,  $C_2H_4 \left( C \begin{smallmatrix} \text{NPh} \cdot \text{NH} \\ \text{N} \text{---} \text{C} \cdot \text{NH} \end{smallmatrix} \right)_2$ , obtained when phenylamidoguanidine hydrochloride and potassium succinate, in molecular proportion, are heated with an excess of succinic chloride, is almost insoluble in water, chloroform, or benzene, and dissolves slightly in alcohol, from which it crystallises in needles melting at  $390^{\circ}$ . Its *picrate*,  $C_{18}H_{18}N_8 \cdot (C_6H_3N_3O_7)_2$ , is moderately soluble in alcohol or chloroform, but only very slightly so in water, ether, or

benzene; it separates from alcohol in beautiful crystals melting and decomposing at  $245^{\circ}$ .

Phenylamidoguanidine hydrochloride and sodium carbonate, when heated with an excess of ethylic oxalate, do not give rise to bis-imido-phenyltriazoline as might be expected, but to phenylimidotriazoline, or, if the temperature is moderated, to oxalylphenylamidoguanidine. The latter forms a *picrate*,  $C_2O_2[NPh \cdot NH \cdot C(NH) \cdot NH_2]_2 \cdot 2C_6H_3N_3O_7$ , which is very soluble in alcohol, and separates from it in crystals melting at  $174^{\circ}$ .  
T. H. P.

**Action of Phosphorus Pentasulphide on Phenyl- and Paratolyl-urazole.** By GUIDO PELLIZZARI and A. A. FERRO (*Gazzetta*, 1898, 28, ii, 541—563).—By the action of phosphorus pentasulphide on many oxygenated organic compounds, products of reduction are obtained as well as sulphur substitution derivatives. Thus Pellizzari and Cuneo (Abstr., 1895, i, 73) found that this reagent reduces urazole to triazole. The authors are of opinion that the oxygen atom is first displaced by sulphur, the reduction taking place subsequently, and they have succeeded in obtaining certain compounds intermediate between the sulphur derivatives and the products of reduction. With 1-phenylurazole, a mixture of three products is obtained by the action of phosphorus pentasulphide.

1-Phenyl-3-thiotriazolone,  $NPh \cdot \begin{smallmatrix} CH:N \\ \diagdown \\ NH \cdot CS \end{smallmatrix}$ , separates from benzene in colourless, lustrous, acicular crystals melting at  $189^{\circ}$ ; it is fairly soluble in alcohol, slightly so in ether, carbon bisulphide, or water, and insoluble in light petroleum; it acts both as an acid, yielding metallic derivatives with the alkali metals, and as a feeble base, forming an unstable hydrochloride. By treatment with phosphorus pentasulphide, it is converted into 3-thio-bis-1-phenyltriazole and 1-phenyltriazole, the former of which is also produced on heating it or on boiling its alcoholic solution. The *silver* derivative of phenylthiotriazolone,  $C_8H_6N_3SAg$ , is a white powder. The *barium* compound,  $(C_8H_6N_3S)_2Ba$ , crystallises in small needles. The authors have established the constitution given above by preparing the same compound synthetically from formic acid and phenylsemithiocarbazide.

3-Thio-bis-1-phenyltriazole,  $S \left( C \begin{smallmatrix} N:CH \\ \diagdown \\ N \cdot NPh \end{smallmatrix} \right)_2$ , is only slightly soluble in any of the ordinary solvents except hot alcohol, from which it crystallises in long, shining, prismatic needles melting without decomposition at  $136^{\circ}$ ; it is insoluble in potash even on heating, but dissolves in boiling hydrochloric acid, giving an unstable hydrochloride separating in white, acicular crystals. By the action of phosphorus pentasulphide, it yields the phenylthiotriazolone described above and 1-phenyltriazole.

By using paratolylurazole in place of the phenyl compound, the following paratolyltriazole derivatives were obtained:

1-Paratolyl-3-thiotriazolone,  $C_7H_7 \cdot N \begin{smallmatrix} CH:N \\ \diagdown \\ NH \cdot CS \end{smallmatrix}$ , is soluble in hot alcohol or benzene, and crystallises from the latter with half a mol. of benzene. It melts at  $218^{\circ}$ , sublimes unchanged at a slightly lower



temperature, and on further heating, gradually decomposes with the evolution of hydrogen sulphide and formation of thio-bis-tolyl-triazole. It dissolves in alkalis and gives white, curdy precipitates with silver nitrate and mercuric chloride, and a bluish-green precipitate with copper sulphate solution. The position of the sulphur atom was established by synthesising the compound from formic acid and *paratolylsemithiocarbazide*,  $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ ; this substance, prepared by the action of ammonium thiocyanate on paratolyl-hydrazine hydrochloride in alcoholic solution, is very soluble in alcohol, fairly so in benzene and ether, and forms shining, hexagonal laminæ melting at  $150^\circ$ . It is only slightly soluble in water, but dissolves readily in dilute solutions of alkalis or mineral acids. With silver nitrate and with yellow mercuric oxide, it gives black precipitates, and in the latter case imparts to the liquid a strong odour of bitter almonds.

3-Thio-bis-1-paratolyltriazole,  $\text{S} \left( \text{C} \begin{smallmatrix} \text{N}:\text{CH} \\ \text{N} \cdot \text{N} \cdot \text{C}_7\text{H}_7 \end{smallmatrix} \right)_2$ , melts at  $188^\circ$ , crystallises from boiling alcohol in beautiful, yellowish needles, and is insoluble in the other ordinary solvents.

1-Paratolyltriazole was also obtained by the action of phosphorus pentasulphide on paratolylurazole. T. H. P.

**Hydromethylmorphimethine.** By EDUARD VONGERICHTEN (*Ber.*, 1899, 32, 1047—1050).—Methylmorphimethine is readily reduced by sodium in alcoholic solution to dihydromethylmorphimethine, whilst codeine, under the same conditions, remains unchanged; it therefore seems probable that the two additional hydrogen atoms in hydromethylmorphimethine are attached to two carbon atoms, between which a double linking has been produced by fission of the codeine ring.

Owing possibly to the conversion of the  $\alpha$ -modification of methylmorphimethine into the  $\beta$ -modification of hydromethylmorphimethine on reduction, the latter substance is stable under conditions in which  $\alpha$ -methylmorphimethine undergoes decomposition. Thus, on heating the hydro-base with acetic anhydride in a closed tube at  $170^\circ$  for 10—12 hours, it is only partially decomposed, and on treating the product with methylic iodide, the *methiodide*,  $\text{C}_{20}\text{H}_{23}\text{NO}_4\text{I}$ , crystallising from water in pale yellow needles and melting at  $265^\circ$ , is obtained. Further, on heating the methohydroxide of the hydro-base with acetic anhydride under the same conditions, only methylic alcohol is eliminated, and the monacetyl derivative is recovered unchanged.

J. F. T.

**Solanine.** By PAUL CAZENEUVE and P. BRETEAU (*Compt. rend.*, 1899, 128, 887—890. Compare *Abstr.*, 1879, 541).—The pulp obtained by grinding together potato seedlings and slaked lime is dried at the ordinary temperature and extracted with cold alcohol (93 per cent.); the alcoholic extract is distilled in a vacuum at  $40$ — $45^\circ$ . The syrupy residue, on cooling, yields a crystalline mass, which is washed with ether and light petroleum, and repeatedly crystallised from alcohol. The product is solanine, and when obtained by this method it crystallises in colourless needles and melts at  $250^\circ$ . It is insoluble

in water and ether, dissolves slightly in cold alcohol, and is more soluble in the warm solvent. Analyses of a specimen dried at  $105^{\circ}$  gave numbers corresponding with those required for the formula  $C_{28}H_{47}NO_{11}$ ; when crystallised from alcohol and dried at ordinary temperatures, the substance contains  $2H_2O$ . Although insoluble in water, the compound readily dissolves in dilute acids; this indicates a basic character, but it is scarcely alkaline to turmeric. On hydrolysis with hydrochloric acid, it is resolved into solanidine and a sugar possessing reducing properties and giving an osazone.

The solanine thus obtained differs from the preparations of earlier investigators in its behaviour towards concentrated mineral acids. With concentrated sulphuric and nitric acids, the base obtained by the authors slowly develops violet and pink colorations respectively; under these conditions, intense violet colorations were immediately produced from the older preparations. The authors' specimen remains colourless when treated with concentrated hydrochloric acid; the other preparations became yellow. Crystals of solanine develop a light green coloration when treated with warm alcoholic sulphuric acid, and the liquid in contact with the crystals acquires a pink tint; a solanine of German origin gave with this reagent a blood-red coloration.

G. T. M.

**Products of Oxidation of Cholic Acid.** By LASSAR-COHN (*Ber.*, 1899, 32, 683—687).—Cholic acid in alkaline solution kept saturated with carbonic anhydride, is oxidised to dehydrocholic acid by permanganate at the ordinary temperature; the yield is poor, however.

Bilianic acid,  $C_{21}H_{31}O_2(COOH)_3$ , is best obtained by dissolving cholic acid, freed from alcohol, in aqueous sodium carbonate, pouring the solution into 2 per cent. potassium permanganate, decolorising after two days with sodium hydrogen sulphite and sulphuric acid, and filtering after a further twenty-four hours; the yield is 53 per cent. The crude product contains about 2 per cent. of isobilianic acid; to remove this, it is treated with boiling baryta water; barium isobilianate is insoluble, the bilianate soluble, in hot water. The acids are recrystallised by dissolving them in a little alcohol and diluting the solution with water.

*Cilianic acid*,  $C_{17}H_{25}O_3(COOH)_3 + H_2O$ , is obtained by dissolving bilianic acid in 12 per cent. caustic soda, adding a dilute solution of potassium permanganate, and boiling vigorously in a flask for twenty minutes or so, until decolorisation is complete. The product of ten such operations was mixed with sodium hydrogen sulphite, and 20 per cent. sulphuric acid, until it was decolorised and acid in reaction; from this solution, the cilianic acid separated in the course of twenty-four hours; it was recrystallised from alcohol and water. It melts at  $242^{\circ}$ , forms a silver salt of apparently abnormal composition, and has about half the normal molecular weight in freezing acetic acid and boiling ethereal solution; this is perhaps due to the fact that it contains  $1H_2O$  which cannot be removed by drying, but is possibly split off in solution. The *trimethylic* salt, prepared from the silver salt and methylic iodide, melts at  $119^{\circ}$ , and has the normal molecular weight in freezing phenol solution.

C. F. B.

## Organic Chemistry.

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**Alkyl, Alphyl, and Arryl.** By DANIEL VORLÄNDER (*J. pr. Chem.*, 1899, [ii], 59, 247).—The author recommends the use of the term alkyl for all univalent hydrocarbon radicles, dividing them further into alphyl or fatty, such as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , &c.; arryl or aromatic, such as  $\text{C}_6\text{H}_5$ ; and alpharryl, aromatic radicles with fatty characters, such as benzyl, nitrobenzyl, &c. He proposes the term acyl as a general term for all acid radicles. F. H. N.

**Action of Nitric Acid and of Nitrosulphuric Acid on Saturated Hydrocarbons.** By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1899, 32, 1441—1445. Compare Francis and Young, *Trans.*, 1898, 73, 928).—All paraffins of the types  $\text{CHR}_2\cdot\text{CHR}_2$  and  $\text{CHR}_3$  (where  $\text{R}=\text{CH}_3$  or any normal alkylic group) are readily acted on by nitric acid of sp. gr. 1.535; oxidation takes place slowly at  $0^\circ$ , but at a slightly higher temperature the reaction is very violent, the chief products being acetic acid and carbonic anhydride together with small quantities of oxalic acid; succinic acid is also formed when small quantities of naphthenes are present. Di-isobutyl, in addition, yields isobutyric acid, and di-isoamyl, a higher fatty acid. Crystalline tertiary nitro-derivatives are also formed, only one of which, *trinitrodimethyl-propylmethane*,  $\text{NO}_2\cdot\text{CMe}_2\cdot\text{C}(\text{NO}_2)_2\cdot\text{CH}_2\text{Me}$ , crystallising in needles and melting at  $95^\circ$ , has been analysed. Di-isobutyl yields a small quantity of a nitro-derivative melting at  $87\text{--}88^\circ$ , probably identical with Francis and Young's trinitrodi-isobutyl melting at  $91^\circ$ . The stability of normal paraffins towards concentrated nitric acid at ordinary temperatures has been confirmed.

Trimethylethylmethane (see following abstract), as a type of the hydrocarbons  $\text{CR}_4$ , is only slowly acted on by nitric acid at the ordinary temperature; it is, however, more readily attacked than normal hexane.

Nitrosulphuric acid, which the author regards as a solution of  $\text{OH}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}_2$  in sulphuric acid, acts quite differently from concentrated nitric acid; a few degrees above  $0^\circ$ , it has practically no action on tertiary hydrocarbons, and the hydrocarbons of lower boiling point may even be distilled over nitrosulphuric acid without undergoing any great decomposition; with aromatic hydrocarbons, nitrosulphuric acid behaves as a stronger oxidising agent than nitric acid itself. Of the naphthenes, hexanaphthene is less readily acted on than its homologues, being quite as stable as normal hexane; penta- and hepta-methylene behave similarly, being oxidised only when heated with the acid and then quite regularly, a dibasic acid containing the same number of carbon atoms as the original hydrocarbon being formed. Methyl- and dimethyl-pentamethylenes, and methyl- and dimethyl-hexanaphthenes are readily attacked by concentrated nitric acid, yielding dibasic acids. The action of nitrosulphuric acid on these cyclic hydrocarbons and on the paraffins is similar. J. J. S.

**Quaternary Paraffins, CR<sub>4</sub>.** By WLADIMIR B. MARKOWNIKOFF (*Ber.*, 1899, 32, 1445—1449).—Trimethylethylmethane occurs in Caucasian naphtha, and is best obtained in a pure form from this source by nitrating the fraction of naphtha boiling at 50—51° three times at 100° with nitric acid of sp. gr. 1.235, and then boiling with acid of sp. gr. 1.4. It is also probably contained in American petroleum. It was proved to be identical with Goriainoff's synthetical hydrocarbon (*Annalen*, 1874, 165, 107), which, however, boils at 49.6—49.7° under 760 mm. pressure, and not, as he stated, at 43—48°; it has a sp. gr. 0.6662 at 0°/0° and 0.6488 at 20°/0°. Further proof of its constitution is given by the fact that its nitro-derivative, when reduced by alkaline stannous chloride, yields an oxime which, on hydrolysis, gives a mixture of ketones from which pinacolone can be isolated. The nitro-derivative,  $\text{CMe}_3 \cdot \text{CHMe} \cdot \text{NO}_2$ , is crystalline, melts at 40°, distils at 167.5—167.8° under 748 mm. pressure, has an odour of camphor, sublimes readily, and is soluble in alcohol, and especially in light petroleum; no trace of a primary nitro-compound is formed when the hydrocarbon is nitrated. When reduced with tin and hydrochloric acid, the amine,  $\text{CMe}_3 \cdot \text{CHMe} \cdot \text{NH}_2$ , boiling at 101.5—102.5° is obtained; its hydrochloride crystallises in small needles, does not melt below 245°, and is readily soluble in water; the platinochloride crystallises in four-sided, orange-coloured prisms or glistening cubes, and is readily soluble in water or alcohol; the aurichloride,  $\text{C}_6\text{H}_{13} \cdot \text{NH}_2, \text{HAuCl}_4$ , is less soluble, and crystallises in needles melting at 186—187° and decomposing at 196°. The same base may be obtained by the reduction of pinacoloxime, which crystallises from light petroleum in large plates melting at 77—78° and boiling at 171.6° under 748 mm. pressure.

Tetramethylmethane is probably contained in the gases from Caucasian naphtha.  
J. J. S.

**Theory of Unsaturated and of Aromatic Compounds.** By JOHANNES THIELE (*Annalen*, 1899, 306, 87—142).—The author holds the view that, in unsaturated compounds, whilst two affinities of every atom which participates in the double linking are occupied with those of the contiguous atom, the combining energy is not completely absorbed, so that the atoms in question still possess valency (*Partialvalenz*), and it is in this partial valency that the source of additive capacity is to be found. The idea may be expressed by the symbols,  $\dots\text{C}=\text{C}\dots$ ,  $\dots\text{C}=\text{O}\dots$ , &c.

It is pointed out that the system  $\text{C}=\text{C}-\text{C}=\text{C}$  takes up hydrogen or bromine at the extremities, becoming  $\text{CH}-\text{C}=\text{C}-\text{CH}$  or  $\text{CBr}-\text{C}=\text{C}-\text{CBr}$ . The central carbon atoms appear to have lost their additive function, which is inconsistent with the scheme  $\dots\text{C}=\text{C}-\text{C}=\text{C}\dots$ ;  
 $\vdots$   
 $\vdots$   
 ; in other words, each has lost its partial valency, which is engaged in balancing that of the other, according to the symbol  $\dots\text{C}=\text{C}=\text{C}=\text{C}\dots$ . A new form of double linking has been thus produced having no partial valency; it is therefore suitably termed inactive (*inactive*). The author refers to systems typified by the foregoing, as conjugated (*conjugirt*).

If the extremities of a conjugated system exert their additive capabilities, the central carbon atoms become active, and their partial valency reappears, as indicated by the symbol

$$\begin{array}{c} \text{CH}-\text{C}=\text{C}-\text{CH} \\ \vdots \quad \vdots \end{array}$$

These principles are applicable to a very large number of chemical changes, but it is not possible to do justice to the discussion in an abstract.

M. O. F.

**Oxidation of Unsaturated Compounds with Potassium Permanganate.** By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1899, [ii], 59, 287—292).—According to Wagner (Abstr., 1890, 1313; 1892, 310, &c.), when unsaturated compounds are oxidised with permanganate, the first action consists in the addition of hydroxyl groups, the number added being equal to that of the atoms of bromine with which the substance is able to combine, the resulting glycol subsequently undergoing further oxidation; he maintains, moreover, that, during the oxidation, neither hydration nor dehydration takes place. Saytzeff (Abstr., 1886, 140) and others have shown, however, that an oxide is probably the first product, and that subsequent hydration may account for the production of a glycol.

The author discusses the question in detail, with special reference to the production of oxoetenol from dimethyltertiarybutylethylene (Butleroff, Abstr., 1878, 121; 1882, 936) and the formation of ecgonine during the oxidation of anhydroecgonine. He holds that oxygen is added first and that then hydration takes place.

A. L.

**Hydrogenation of Acetylene in Presence of Nickel.** By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1899, 128, 1173—1176).—When mixtures of acetylene and hydrogen are passed over finely divided, reduced nickel at the ordinary temperature, interaction takes place and heat is developed, so that the temperature of the metal gradually rises. The chief reaction is the formation of ethane, but the composition of the crude product depends on the relative proportions of acetylene and hydrogen, the temperature, and the velocity of the gaseous current. Ethylene is formed in considerable quantity, together with liquid products consisting chiefly of paraffins with some olefines, and a small quantity of benzene. The proportion of liquid products is greater the higher the temperature and the lower the proportion of hydrogen present. As the proportion of acetylene in the original gaseous mixture is increased, the proportion of benzene hydrocarbons in the product also increases until eventually the metal intumescs and becomes incandescent, as Moissan and Moureu observed with pure acetylene and nickel (Abstr., 1898, i, 585).

The nickel undergoes no change, except that a small quantity of carbon is deposited on it.

Iron, cobalt, and copper behave similarly, and these facts may throw light on the origin of petroleum.

C. H. B.

**Action of Bromine on  $\alpha\beta$ -Propylenic Bromide in Presence of Anhydrous Aluminium Bromide: Preparation of  $\alpha\alpha\beta$ -Tri-bromopropane.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], 19, 805—807).—A solution of aluminium bromide in bromine was gradually added to a mixture of  $\alpha\beta$ -propylenic bromide with bromine,

maintained at about  $25^{\circ}$ , and the product subsequently thrown into cold, dilute hydrobromic acid. The oily liquid which separated, on fractional distillation under diminished pressure, gave (1) 65—70 per cent. of the theoretical yield of a substance which, by analysis and by its conversion into monobromopropylene,  $\text{CHMe}\cdot\text{CHBr}$ , when treated with zinc powder in alcoholic solution, was proved to be  $\alpha\alpha\beta$ -tribromopropane,  $\text{CHMeBr}\cdot\text{CHBr}_2$ ; (2) a small quantity, never exceeding 7—8 per cent., of a liquid having the composition of a tribromopropane, which yields triacetin when heated with silver acetate at  $110^{\circ}$ , and is, therefore, regarded as tribromhydrin,  $\text{H}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ ; (3) a very small quantity of  $\alpha\alpha\beta\gamma$ -tetrabromopropane (see following abstract). N. L.

**Action of Bromine on  $\alpha\alpha\beta$ -Tribromopropane and on Tribromhydrin in Presence of Aluminium Bromide: Preparation of  $\alpha\alpha\beta\gamma$ -Tetrabromopropane.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], 19, 807—810).—A solution of aluminium bromide in bromine was gradually added to a mixture of  $\alpha\alpha\beta$ -tribromopropane with bromine maintained at a temperature of about  $50^{\circ}$ . The product, when fractionally distilled, yielded 60—65 per cent. of a heavy liquid boiling at  $138$ — $140^{\circ}$  under 17 mm. pressure and having the composition of a tetrabromopropane, together with a smaller quantity of a heavy liquid boiling at  $165$ — $175^{\circ}$  under 17 mm. pressure, which proved to be a pentabromopropane. The tetrabromopropane thus obtained has in all probability the constitution represented by the formula  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CHBr}_2$ , since it is identical with the product of the action of bromine on  $\beta$ -epidibromhydrin,  $\text{CH}_2\text{Br}\cdot\text{CH}\cdot\text{CHBr}$ , and also with the tetrabromopropane formed by the bromination of tribromhydrin,  $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , in presence of aluminium bromide. It becomes viscous, but does not crystallise, when cooled to the boiling point of methylic chloride, and is converted by heating with an alcoholic solution of potassium acetate into a tribromopropane boiling at  $210$ — $220^{\circ}$ , which reacts with bromine in sunlight to form a liquid pentabromopropane.

The pentabromopropane which, as stated above, is formed by the action of bromine on tribromopropane, is more readily obtained by brominating  $\alpha\alpha\beta\gamma$ -tetrabromopropane. It was not prepared in sufficient quantity to allow of its constitution being definitely established, but as the central carbon atom in the halogen derivatives of propane is brominated with most difficulty, it probably has the formula  $\text{CHBr}_2\cdot\text{CHBr}\cdot\text{CHBr}_2$ . N. L.

**Behaviour of Tetramethylethylenic Dibromide towards Alcoholic Potash.** By IWAN L. KONDAKOFF (*J. pr. Chem.*, 1899, [ii], 59, 293—301).—The author has repeated Couturier's work on the action of alcoholic potash on tetramethylethylenic dibromide. The product has an odour of allene and of ethylic valerate, and so far from being a pure substance, as stated by Couturier, is divisible into four fractions; about two-thirds boils at  $69$ — $74^{\circ}$ , a very small quantity at  $74$ — $130^{\circ}$ , a small quantity at  $130$ — $140^{\circ}$ , and the portion of higher boiling point sets to a mass of needles.

The fraction  $69$ — $74^{\circ}$  has a sp. gr. 0.7350 at  $0^{\circ}$ , and 0.7077 at  $18^{\circ}$ ,

and a molecular refractive power 29.32 for sodium light. (Calculated for  $C_6H_{12}$  with one ethylenic union  $[M]_D = 29.4$ ). It absorbs bromine in ethereal solution at  $-10^\circ$ , yielding a mixture of crystalline substances, and also forms compounds with hydrogen chloride. The crystalline residue, which at first melted at  $152^\circ$ , appeared to be a mixture of at least two substances.

It is concluded that Couturier's product is a mixture of at least two hydrocarbons, namely, tetramethylethylene, and either di-isopropenyl or a cyclic hydrocarbon. The author finally gives his view of the nature of the changes which take place during the production of the mixture.

A. L.

**Action of Cuprous Chloride on Nitriles.** By CH. RABAUT (*Bull. Soc. Chim.*, 1898, 19, [iii], 785—788).—Cuprous chloride and the nitriles do not react in the presence of ammonia, but combination takes place in cold hydrochloric acid solutions. The substances produced are insoluble in water or the neutral solvents, and form colourless crystals which readily oxidise on exposure to air. Hydrogen cyanide is completely absorbed by a saturated solution of the chloride in hydrochloric acid; the resulting compound has the composition  $HCN, Cu_2Cl_2, 2HCl$ . Acetonitrile similarly treated yields the compound  $2CH_3 \cdot CN, Cu_2Cl_2$ . Propionitrile and its higher homologues are more or less hydrolysed by this reagent, and do not yield compounds of this type. The substance  $C_2N_2, 2Cu_2Cl_2$  is obtained from cyanogen, whilst succinonitrile gives rise to  $2CH_2(CN)_2, Cu_2Cl_2$ . Benzonitrile and phenylacetoneitrile yield  $2CNPh, Cu_2Cl_2$  and  $4C_6H_5 \cdot CH_2 \cdot CN, Cu_2Cl_2$  respectively. The substance  $C_6H_4Me \cdot CN, Cu_2Cl_2$  is obtained from orthotoluonitrile, and the para-compound gives  $2C_6H_4Me \cdot CN, Cu_2Cl_2$ , but the meta-isomeride does not react with cuprous chloride. 2:4-Dimethylbenzonitrile produces the compound,  $2C_6H_3Me_2CN, Cu_2Cl_2$ .  $\alpha$ - and  $\beta$ -Naphthonitriles yield white, crystalline compounds,  $2C_{10}H_7 \cdot CN, Cu_2Cl_2$ . Substituted nitriles do not react with cuprous chloride, and negative results were obtained with the following compounds: cyanacetic acid, glycollonitrile, propionylpropionitrile, amygdalin, and the para- chloro-, bromo-, and nitro-derivatives of benzonitrile. These additive products may also be obtained by warming dry cuprous chloride with the nitrile; should the latter be a solid, combination may be effected in alcoholic solution. This property of the nitriles may be employed in their isolation and purification: a solution containing a nitrile is treated with a cold saturated hydrochloric acid solution of cuprous chloride, and the precipitate collected and washed with alcohol; the nitrile is regenerated from the additive product by decomposing the latter with either ferric chloride or hydrogen sulphide, and extracted by means of an appropriate solvent; the former method of decomposition seems to give the better results.

G. T. M.

**Formation of Potassium  $\beta$ -Ferriecyanide through the Action of Acids on the Normal Ferriecyanide.** By JAMES LOCKE and GASTON H. EDWARDS (*Amer. Chem. J.*, 1899, 21, 413—418. Compare Abstr., 1899, i, 407).—The use of an oxidising agent in the preparation of potassium  $\beta$ -ferriecyanide from the normal ferriecyanide is found to be unnecessary; the change is due to the hydrochloric acid used,

and may be effected by the use of small quantities of mineral acids. Even feeble acids, such as oxalic or acetic acids, are capable of inducing the transformation; the velocity of the change, however, diminishes with decrease in ionisation of the acid used. A. L.

**Cyanuric Compounds.**—By OTTO DIELS (*Ber.*, 1899, 32, 1219—1220).—The compound previously described as diamidocyanuric hydride (compare this vol., i, 406) is identical with Nencki's formoguanamine (this Journal, 1875, 754). The substance melts, however, at 329° (corr.), although it is stated by Nencki not to melt below 350°. The formation of formoguanamine from cyanuric chloride affords a further proof of the constitution of the former compound (Weith, *Ber.*, 1876, 9, 460). A. H.

**Methylic Phosphates.** By JACQUES CAVALIER (*Bull. Soc. Chim.*, 1898, [iii], 19, 883—887).—Monomethylic and dimethylic phosphates are readily obtained by the action of phosphoric anhydride on methylic alcohol in ethereal solution, the two acids being separated by conversion into their barium salts, which differ greatly in solubility. If the quantity of phosphoric anhydride employed is rather less than that corresponding with the formation of the dimethylic phosphate, a yield of about 65 per cent. of monomethylic and 30 per cent. of dimethylic phosphate is obtained.

*Barium methylic phosphate*,  $\text{PO}_4\text{MeBa} + \text{H}_2\text{O}$ , crystallises in white scales which become anhydrous at 100°, and are less soluble in hot than in cold water, one hundred grams of the solution containing 1.83 grams of the anhydrous salt at 15°, 1.42 grams at 40°, and 0.62 gram at 70°. Like the analogous ethylic and allylic derivatives, monomethylic phosphate is rendered neutral to methyl-orange by addition of 1 mol. of alkali, whereas if phenolphthalein is employed as the indicator, the neutral point is only reached when 2 mols. of alkali have been added. By taking advantage of these facts, a number of acid salts of the general formula  $\text{PO}_4\text{MeMH}$  have been prepared; these are all neutral to methyl-orange, but acid to phenolphthalein. The *barium* salt,  $(\text{PO}_4\text{MeH})_2\text{Ba} + \text{H}_2\text{O}$ , is much more soluble in water than the normal salt described above, one hundred grams of the solution containing 23.1 grams of the anhydrous salt at 15°, 24.0 grams at 36°, 24.7 grams at 60°, 26.5 grams at 73°, and 28.6 grams at 85°. The *strontium* salt crystallises, like the barium salt, with  $\text{H}_2\text{O}$ , whereas the calcium salt is anhydrous, as also are the *potassium*, *ammonium*, and *sodium* salts. These are all soluble, crystalline compounds which lose methylic alcohol on ignition, and leave a residue of metaphosphate.

*Barium dimethylic phosphate*,  $(\text{PO}_4\text{Me}_2)_2\text{Ba}$ , is obtained in the preparation of the methylic phosphates as an indefinitely crystalline mass very soluble in water. The *lead* salt forms colourless, slender needles, which are more soluble in hot than in cold water, melt at 155°, and decompose at about 225° with the production of trimethylic phosphate. Dimethylic hydrogen phosphate is most conveniently prepared by decomposing the lead salt with hydrogen sulphide. N. L.

**Preparation of Mixed Ethers.** By ARNOLD H. PETER (*Ber.*, 1899, 32, 1418—1421).—When a mixture of amylic alcohol (boiling



at 132—133°) and ethylic alcohol is mixed with an equal weight of 85 per cent. sulphuric acid, and the temperature of the whole maintained at 135—140° while more of the alcoholic mixture is run in, but little sulphurous anhydride is evolved, and the distillate, when washed and distilled twice over solid caustic potash, boils at 40—180°. On fractionation, a considerable portion boils at 79—81°; this undoubtedly contains ethylic alcohol, but the greater part of it does not dissolve in water, and is found to be ethylic amylic ether, boiling at 112° and of sp. gr. 0.761 at 18°. The fraction which boils at 81—130° contains ethylic amylic ether, amylic alcohol, and diamylic ether; on the small scale, the alcohol is best removed by treatment with 85 per cent. sulphuric acid, after which the ethers may be separated by fractional distillation.

These results confirm those of Williamson (*Annalen*, 1851, 77, 37; 1852, 81, 73). Guthrie (*ibid.*, 1858, 105, 37) and Norton and Prescott (Abstr., 1885, 496) have doubted the possibility of obtaining ethylic amylic and methylic amylic ethers by the process in question; they probably used acid of too great strength. C. F. B.

**Dextrins of Saccharification.** By PAUL PETIT (*Compt. rend.*, 1899, 128, 1176—1178).—The action of amylase on starch at 70° yields a dextrin,  $(C_6H_{10}O_5)_3$ , with a rotatory power  $\alpha_D = 166.6$  and a reducing power equivalent to 18 per cent. of maltose. Prolonged action of the amylase partially converts it into maltose. With barium hydroxide, it yields the compound  $2C_6H_{10}O_5 \cdot C_6H_8O_5Ba$ . The action of amylase on various worts yields dextrins which form barium compounds corresponding with the molecular formulæ  $(C_6H_{10}O_5)_2$ ,  $(C_6H_{10}O_5)_4$ , and  $(C_6H_{10}O_5)_5$ . *Penicillium glaucum* and *Aspergillus niger* in active growth, and the liquid pressed out from yeast, also have the property of partially converting dextrin into maltose.

C. H. B.

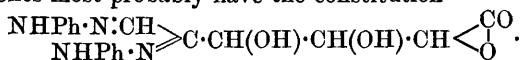
**Nitrocellulose.** By GEORG LUNGE and E. WEINTRAUB (*Zeit. angew. Chem.*, 1899, 441—448, 467—475).—By the action of concentrated nitric acid on a solution of cellulose in concentrated sulphuric acid, a substance is obtained which is soluble in acetone, ethylic acetate, methylic and ethylic alcohols, and in concentrated nitric acid. This compound contains nitrogen corresponding in amount with that required for a pentanitrocellulose, and is possibly a pentanitrocellulose-dextrin or a pentanitramyloid. By increasing the proportion of sulphuric acid to nitric acid in the ordinary process of nitration, the velocity of the reaction is very greatly decreased, and the product contains less nitrogen; when the ratio of the sulphuric acid to the nitric acid is 8 to 1 or more, some of the cellulose is not attacked. Nitration takes place much more rapidly at higher temperatures, but there is a greater loss of material by solution in the acid; the nitrocellulose obtained by nitrating at 40° contains less nitrogen than that prepared at the ordinary temperature. The presence of nitric peroxide in the nitric acid used for nitration has apparently little or no effect until its amount reaches 12 per cent., when the degree of nitration effected is slightly diminished. The highest nitrated products, when examined under the microscope in polarised light, have a characteristic light or

dark blue appearance, but it is impossible to distinguish hexanitrocellulose from pentanitrocellulose. As the percentage of nitrogen decreases, the blue gradually fades into grey. The presence of cellulose in the product is easily detected by the brilliant yellow to reddish coloration, but the intensity of the coloration does not afford a trustworthy indication of the quantity present. To determine the amount of free cellulose, about 5 grams of the nitrocellulose are heated at 40—50° for 20—30 minutes with 150 c.c. of a mixture of 100 c.c. of acetone with 100 c.c. of ordinary alcohol in which 2—3 grams of sodium have been dissolved. The nitrocellulose is destroyed by sodium methoxide or ethoxide, and also, but more slowly, by sodium amylxide. The brown, insoluble residue is washed with alcohol and water by decantation, collected, and finally washed with hot water containing a little hydrochloric acid; it still contains traces of nitrocellulose, which may be removed by repeating the process. The cellulose obtained is colourless when wet, but very slightly yellow when dry; the colour may be removed by means of bleaching powder.

E. W. W.

**Oxycellulose Osazones.** By LÉO VIGNON (*Compt. rend.*, 1899, 128, 1038—1040).—Phenylhydrazine combines with oxycellulose in presence of acetic acid, but the quantity which enters into combination varies with the nature of the oxycellulose, and is higher the more completely the cellulose has been oxidised. The action of potassium chlorate and hydrochloric acid, or of chromic acid and dilute sulphuric acid for not too long a time, gives the best results, and the product combines with about 8 per cent. of phenylhydrazine. The tendency of the oxycelluloses to combine with phenylhydrazine varies in the same order as their tendency to yield furfuraldehyde (*Abstr.*, 1898, i, 620).

The osazones most probably have the constitution



C. H. B.

**The So-called Lignin Reaction of Wood.** By FRIEDRICH CZAPEK (*Zeit. physiol. Chem.*, 1899, 27, 141—166).—An historical survey of the more important researches on the constituents and colour reactions of woody tissues. A substance termed *hadromal* has been isolated from different woody tissues; it has the properties of a phenol and of an aldehyde, is probably a para-compound, and is regarded as the active principle which causes the more characteristic colorations of woody tissues. Minute quantities of this principle appear to be extracted when finely-divided wood is treated with boiling benzene, alcohol, or ether, since the solutions thus obtained give the same colour reactions as the wood itself. A somewhat larger quantity is obtained when the woody tissue is first heated with stannous chloride for about three hours and then extracted with benzene. It is best purified by solution in light petroleum, conversion into its sodium hydrogen sulphite compound, and finally by several recrystallisations from light petroleum, when it is obtained as a pale yellowish-brown, crystalline powder which gives the lignin reactions of wood in a marked degree. The

compound has not been obtained quite pure, and has not been analysed. It has an aromatic odour, sinters at 50—60°, and melts at 75—80°. It does not contain nitrogen, is sparingly soluble in hot water, readily in alcohol and most organic solvents, also in alkalis; it is not volatile with steam, and has the properties of an aldehyde and also of a phenol. Its benzoyl derivative and phenylhydrazone have been prepared, but not examined. The amount present is not more than 1—2 per cent. of the dry woody tissue, and it is thought that although a part of the compound exists in the free state, the greater part is in combination as a hadromal-cellulose, which becomes decomposed by the stannous chloride. J. J. S.

**Action of Nitrosyl Chloride on Fatty Amines. III. Primary Diamines.** By WASSILY A. SOLONINA (*Chem. Centr.*, 1899, i, 25—27; from *J. Russ. Chem. Soc.*, 1898, 30, 606—632. Compare this vol., i, 473).—By mixing cooled solutions of nitrosyl chloride and ethylenediamine in metaxylene, nitrogen is evolved and a white precipitate of salts formed. After treating with water, the dry metaxylene solution yields ethylenic chloride, which, by the action of sodium phenoxide, forms diphenoxyethane,  $C_2H_4(OPh)_2$ , melting at 97—98°.

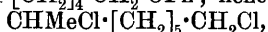
When ethereal solutions of nitrosyl chloride and hexamethylenediamine,  $C_6H_{12}(CH_2 \cdot NH_2)_2$ , are mixed at 0°, nitrogen is liberated and a white precipitate formed. By treating the product with water, removing the ether, distilling first with steam and then under reduced pressure, a fraction boiling at 200—205° or at 85—105° under 25—30 mm. pressure is obtained. It has the composition of a hexylenic chloride,  $C_6H_{12}Cl_2$ , but contains two isomerides and a small quantity of an unsaturated compound. When treated with sodium phenoxide and distilled with steam, *phenoxyhexylene*,



formed mainly from the hexylenic chloride, is obtained; this substance may also be prepared by the action of sodium phenoxide on methylpentamethylene bromide,  $CHMeBr \cdot [CH_2]_3 \cdot CH_2Br$ , and boils at 200—205°. The residue from the distillation in steam, when treated with potassium hydroxide and extracted with ether, yields 1:5-diphenoxyhexane,  $OPh \cdot CHMe \cdot [CH_2]_3 \cdot CH_2 \cdot OPh$ , as an oil, and 1:6-diphenoxyhexane,  $OPh \cdot CH_2 \cdot [CH_2]_4 \cdot CH_2 \cdot OPh$ . The former indicates the production of methylpentamethylene chloride in the original reaction. The latter crystallises in monoclinic prisms (Popoff), melts at 82.5°, dissolves sparingly in cold water but easily in hot alcohol, benzene or ether; when treated with hydrochloric acid at 165—175°, it forms hexamethylenic chloride boiling at 203—205°, hence this compound is probably a product of the original reaction. An unsaturated chloro-compound, probably  $CHMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_2Cl$ , is also obtained.

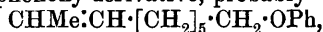
By the action of nitrosyl chloride on heptamethylenediamine, compounds similar to those obtained in the case of hexamethylenediamine are formed, but only *heptamethylene chloride*,  $C_7H_{14}(CH_2Cl)_2$ , was identified by means of the diphenoxy-derivative, which melts at 54.5—55°, is easily soluble in benzene and alcohol, and when heated with hydrobromic acid at 160—170°, yields heptamethylene bromide.

By the action of nitrosyl chloride on octomethylenediamine, a distillate boiling at 132—138° under 20—25 mm. pressure is obtained; it contains several compounds, for by the action of sodium phenoxide it yields an *unsaturated monophenoxy-derivative* together with a liquid and a solid crystalline *diphenoxyoctane*,  $C_8H_{16}(OPh)_2$ . The unsaturated compound is easily volatile in steam, boils at 282—286°, combines with bromine, does not form an insoluble, amorphous compound with sulphurous anhydride, and has probably therefore the constitution  $CHMe:CH \cdot [CH_2]_4 \cdot CH_2 \cdot OPh$ ; hence a chloride,



is possibly formed in the original reaction. The liquid diphenoxy-derivative is probably 1:7-*diphenoxyoctane*, is not volatile in steam, boils at 240—250° under 20—25 mm. pressure, and is probably formed from methylheptamethylene chloride,  $CHMeCl \cdot [CH_2]_5 \cdot CH_2Cl$ . The crystalline diphenoxyoctane, derived from octomethylene chloride in the original product, crystallises in small plates, is not volatile in steam, melts at 83·5—84°, and is easily soluble in hot alcohol and in ether or benzene; it combines with hydrogen bromide to form the bromide,  $CH_2Br \cdot [CH_2]_6 \cdot CH_2Br$ , which melts at 15—16°, boils at 150—161° under 20—25 mm. and at 270—272° under the ordinary pressure, with slight decomposition. The corresponding chloride boils at 240—242°.

By the action of nitrosyl chloride on nonomethylenediamine, compounds similar to those obtained in the preceding cases are formed. The products of the reaction, when treated with sodium phenoxide, give (1) an unsaturated phenoxy-derivative, probably



which combines with bromine, is volatile in steam, and dissolves easily in alcohol, ether, or benzene, and (2) *diphenoxynonane*,



which crystallises in white leaflets, melts at 62°, is not volatile in steam, is soluble in hot alcohol, ether, or benzene, and combines with hydrogen bromide to form nonomethylene bromide boiling at 285—288°, with liberation of hydrogen bromide, and at 171—173° under 20—25 mm. pressure. By the action of hydrochloric acid on diphenoxynonane, *nonomethylene chloride* is formed; it is a colourless liquid, boils at 258—262° with partial decomposition, and is easily volatile in steam.

The action of nitrosyl chloride on diamines is similar to that on monamines, nitrogen being liberated and dichloro-derivatives formed, possibly by means of the intermediate production of tetrazo-compounds. The formation of isomerides and of unsaturated compounds, however, is much more marked than in the case of monamines, and nitroso-compounds are probably also produced.

This reaction affords a method of preparing dihalogen derivatives from diamines, for although the yield is poor, it compares favourably with the methods of Geuther, Simonini, &c.

E. W. W.

**Stereochemistry of Nitrogen Compounds.** By CARL D. HARRIES and TAMEMASA HAGA (*Ber.*, 1899, 32, 1191—1199. Compare *Abstr.*, 1898, i, 293).—When the hydrochloride of either of the stereoisomeric

2 : 4-diaminopentanes is heated with fused sodium acetate, it yields an *ethenyl* derivative,  $\text{CH}_2 < \begin{smallmatrix} \text{CHMe} \cdot \text{NH} \\ \text{CHMe} - \text{N} \end{smallmatrix} > \text{CMe}$ . That from the labile  $\alpha$ -base crystallises in thin plates, melts at  $73^\circ$ , is very hygroscopic, has a strongly alkaline reaction, absorbs carbonic anhydride from the air, and forms a crystalline *nitrate* melting at  $194^\circ$ , a *sulphate*, and a *hydrochloride*. That from the stable  $\beta$ -base is similar in properties, but melts at  $102^\circ$ , whilst the nitrate melts at  $250^\circ$ . On boiling  $\alpha$ -diaminopentane with sodium and alcohol, it is converted into the  $\beta$ -base.

T. M. L.

**Synthesis of Glycocine.** By PAUL BOURCET (*Bull. Soc. Chim.*, 1898, [iii], 19, 1005—1006).—Harting (*J. pr. Chem.*, 46, 1) has shown that ethylic chloracetate interacts with hexamethylenamine forming a compound of the formula  $\text{CO} < \begin{smallmatrix} \text{CH} \cdot \text{C}_6\text{H}_{12}\text{N}_4\text{Cl} \\ \text{C}_6\text{H}_{12}\text{N}_4 \end{smallmatrix}$ , and it is now found that a good yield of glycocine is obtained when this substance is heated with a mixture of alcohol and hydrochloric acid according to the general method for the preparation of amines suggested by Delépine (*Abstr.*, 1897, i, 394).

N. L.

**Chrysean.** By GUSTAF HELLSING (*Ber.*, 1899, 32, 1497—1498).—Chrysean, which has been prepared by Wallach (this Journal, 1874, 1086) by passing hydrogen sulphide into a saturated solution of potassium cyanide, may be obtained by the action of concentrated potassium cyanide on thioformamide (Hofmann, *Abstr.*, 1878, 396). From this method of formation, the author deduces the constitution  $\text{NH}[\text{CH}(\text{CN}) \cdot \text{SH}]_2$  for the substance.

J. J. S.

**Chlorophosphines of the Aliphatic Series.** By FR. GUICHARD (*Ber.*, 1899, 32, 1572—1581).—Monalkyldichlorophosphines of the type  $\text{R} \cdot \text{PCl}_2$  are best prepared by heating together a mixture of the mercuryalkyl and phosphorus trichloride in a sealed tube for 6 hours at  $250^\circ$ , at which temperature the alkyl mercurichloride which is formed in the reaction, and which not only makes the product difficult to purify but is dangerous to health, is entirely decomposed into calomel and the hydrocarbon. The monalkyldichlorophosphines are clear, mobile liquids of sharp, unpleasant odour, which are decomposed by water, and in the presence of moisture are coloured yellow.

*Ethylchlorophosphine*,  $\text{PEtCl}_2$ , boils at  $114$ — $117^\circ$ , and has a sp. gr. 1.2952 at  $19^\circ$ .

*Propylchlorophosphine*,  $\text{PPr}^a\text{Cl}_2$ , boils at  $140$ — $143^\circ$ , and has a sp. gr. 1.1771 at  $19^\circ$ .

*Isopropylchlorophosphine*,  $\text{PPr}^b\text{Cl}_2$ , boils at  $135$ — $138^\circ$ , and has a sp. gr. 1.2181 at  $23^\circ$ .

*Isobutylchlorophosphine*,  $\text{C}_4\text{H}_9 \cdot \text{PCl}_2$ , boils at  $155$ — $157^\circ$ , and has a sp. gr. 1.1236 at  $23^\circ$ .

*Isoamylchlorophosphine*,  $\text{C}_5\text{H}_{11} \cdot \text{PCl}_2$ , boils at  $180$ — $183^\circ$ , and has a sp. gr. 1.1024 at  $23^\circ$ .

Monalkylphosphinous acids of the type  $\text{R} \cdot \text{PO}_2\text{H}_2$  are prepared from the chlorophosphines by decomposition with water; they are

colourless syrups which solidify below  $0^{\circ}$ , and are moderately soluble in water; they are monobasic, and evidently have the structural formula  $O\cdot PHR'\cdot OH$ .

*Ethylphosphinous acid*,  $PO_2H_2Et$ , has a sp. gr. 1.2952 at  $19^{\circ}$ .

*Propylphosphinous acid*,  $PO_2H_2Pr^a$ , has a sp. gr. 1.1418 at  $13^{\circ}$ .

*Isopropylphosphinic acid*,  $PO_2H_2Pr^b$ , has a sp. gr. 1.1891 at  $19^{\circ}$ .

*Isobutylphosphinic acid*,  $C_4H_9\cdot PO_2H_2$ , has a sp. gr. 1.0740 at  $23^{\circ}$ .

*Isoamylphosphinic acid*,  $C_5H_{11}\cdot PO_2H_2$ , has a sp. gr. 1.0613 at  $23^{\circ}$ ; the ammonium salt,  $C_5H_{11}PO_2H\cdot NH_4$ , and the iron salt,  $(C_5H_{11}PO_2H)_3Fe$ , are described.

Monalkyltetrachlorophosphines of the type  $R\cdot PCl_4$  are prepared by passing chlorine into the corresponding chlorophosphine. They are yellowish-white substances, closely resembling phosphorus pentachloride in appearance, and rapidly change to the oxychlorophosphine on exposure to the air; with inorganic chlorides, as, for instance, antimony pentachloride, they combine, with the formation of double compounds of the type  $PRCl_4\cdot SbCl_5$ , and with bromine vapour to form white, hygroscopic solids of the type  $PRCl_2Br_2$ .

Monalkyloxychlorophosphines,  $R\cdot PCl_2O$ , are best prepared by acting on the above-mentioned tetrachlorides with sulphurous anhydride; they are colourless or faintly yellow liquids of less unpleasant odour than the chlorophosphines.

*Ethyloxychlorophosphine*,  $EtPOCl_2$ , boils at  $75-78^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.1883 at  $20^{\circ}$ .

*Propyloxychlorophosphine*,  $Pr^aPOCl_2$ , boils at  $88-90^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.3088 at  $20^{\circ}$ .

*Isopropyloxychlorophosphine*,  $Pr^bPOCl_2$ , boils at  $82-84^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.3018 at  $20^{\circ}$ .

*Isobutyloxychlorophosphine*,  $C_4H_9POCl_2$ , boils at  $104-108^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.2333.

*Isoamyloxychlorophosphine*,  $C_5H_{11}POCl_2$ , boils at  $122-125^{\circ}$  under 55 mm. pressure, and has a sp. gr. 1.1883 at  $20^{\circ}$ .

The monalkylthiochlorophosphines of the type  $R\cdot PSCl_2$  can be prepared from the corresponding chlorophosphines by heating in a sealed tube with sulphur for 2-3 hours at  $120-125^{\circ}$ ; they are transparent, yellow liquids of strong odour, and are stable in the presence of water.

*Ethylthiochlorophosphine*,  $EtPSCl_2$ , boils at  $80-82^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.3606 at  $70^{\circ}$ .

*Propylthiochlorophosphine*,  $Pr^aPSCl_2$ , boils at  $95-98^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.2854 at  $20^{\circ}$ .

*Isobutylthiochlorophosphine*,  $C_4H_9PSCl_2$ , boils at  $110-113^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.2515 at  $20^{\circ}$ .

*Isoamylthiochlorophosphine*,  $C_5H_{11}PSCl_2$ , boils at  $130-132^{\circ}$  under 50 mm. pressure, and has a sp. gr. 1.1771 at  $20^{\circ}$ .

Monalkylphosphinic acids of the type  $R\cdot PO(OH)_2$  have already been prepared by von Hofmann; in this case, they were obtained either by oxidising the corresponding phosphinic acid with nitric acid, or by treating the tetrachloro- or the oxychloro-phosphine with water.

Ethylphosphinic acid melts at  $44^{\circ}$ , propylphosphinic acid at  $66^{\circ}$ ,

isopropylphosphinic acid at  $71^\circ$ , isobutylphosphinic acid at  $124^\circ$ , and isoamylphosphinic acid at  $166^\circ$ .

They are white, glistening, crystalline compounds which feel somewhat greasy when touched.

The *phenylic* salt of isoamylphosphinic acid is a heavy liquid, which is not decomposed by water; the *hydrazide*,  $C_5H_{11}PO(N_2H_2Ph)_2$ , is a light, white powder readily soluble in ether and alcohol, and melts at  $134\text{--}135^\circ$ ; the *anhydride*,  $C_5H_{11}PO_2$ , is formed when isoamyloxychlorophosphine reacts with isoamylphosphinic acid in dry light petroleum solution; it consists of small, hard crystals which melt at  $122^\circ$ .

Monalkylthiophosphinic acids of the type  $R\cdot PS(OH)_2$  cannot be obtained pure; the following derivatives were, however, prepared:

*Ethylic monoisoamylthiophosphinite*,  $C_5H_{11}PS(OEt)_2$ , is a transparent, light yellow liquid of peculiar odour boiling at  $250\text{--}255^\circ$ , and of sp. gr. 0.9848 at  $20^\circ$ , *monoisobutylsulphophosphinic phenylhydrazide*,  $C_4H_9PS(N_2H_2Ph)_2$ , forms white leaflets melting at  $128^\circ$ .

J. F. T.

**Oxidation of Formaldehyde by Hydrogen Peroxide.** By J. H. KASTLE and A. S. LOEVENHART (*J. Amer. Chem. Soc.*, 1899, 21, 262—276).—The oxidation of formaldehyde by hydrogen peroxide takes place only extremely slowly at atmospheric temperatures, but with very great velocity at  $100^\circ$ . The velocity coefficient in minutes in half-normal solution was found to be 0.0000189 at  $40^\circ$ , 0.000251 at  $60^\circ$ , 0.00253 at  $80^\circ$ , and 0.0116 at  $98^\circ$ . The influence of light is only slight at low temperatures and above  $90^\circ$ , but has a very marked influence at intermediate temperatures; thus, in direct sunlight, the average velocity constant was 0.0000378 at  $40^\circ$  and 0.000308 at  $60^\circ$ . Acids have a slight accelerating influence on the oxidation, but bases have an enormous effect, so that the addition of  $N/4$  potassium or sodium hydroxide causes the reaction to be completed in about 20 minutes at ordinary temperatures. A method is thus afforded of determining the degree of hydrolysis of salt solutions; thus, whilst sodium chloride had no influence on the velocity of change at  $50^\circ$ , sodium acetate has a great accelerating effect; comparative experiments showed that, at  $60^\circ$ , 1 c.c. of  $N$  sodium acetate had a greater accelerating effect than 1 c.c. of  $N/100$  potassium hydroxide, indicating that the acetate is hydrolysed to the extent of over 1 per cent.

T. M. L.

NOTE.—The authors state “during the progress of the reaction with bases, considerable effervescence occurred due to escaping oxygen.” Blank and Finkenbeiner (*Ber.* 1898, 31, 2980) and Harden have shown (*Proc.*, 1899, 15, 158) that hydrogen is evolved when the reaction takes place in strongly alkaline solution, the gas, according to Harden, being pure if the formaldehyde is in excess, but mixed with oxygen if the hydrogen peroxide is in excess.—EDITORS.

**Preparation of Acraldehyde.** By ALFRED WOHL and L. NEUBERG (*Ber.*, 1899, 32, 1352—1354).—The method of preparing acraldehyde, which depends on the dehydrating action of potassium hydrogen sulphate, has the disadvantage of giving rise to sulphuric acid, which

exerts an oxidising action, and yields sulphurous anhydride. The authors, therefore, substitute boric anhydride or boric acid.

M. O. F.

**Behaviour of Mesitylic Oxide towards Sodium Hydrogen Sulphite.** By CARL D. HARRIES (*Ber.*, 1899, 32, 1326—1330).—Pinner has observed that mesitylic oxide gradually dissolves in a solution of sodium hydrogen sulphite, and is not precipitated again as such from the solution; on neutralising the liquid with sodium carbonate, evaporating to dryness, and extracting the residue with alcohol, the latter deposits the compound  $\text{SO}_3\text{Na} \cdot \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{COMe} + \text{H}_2\text{O}$  as a hygroscopic, crystalline mass.

The author finds that when commercial mesitylic oxide, purified by slow distillation under highly reduced pressure, is vigorously agitated with an aqueous 40 per cent. solution of sodium hydrogen sulphite, 60 per cent. of the ketone is dissolved within 24 hours; the absorption then slackens, and a portion remains undissolved after one week, even when the sulphite solution is renewed. The closest comparison of this portion with the regenerated ketone has failed to reveal any difference between them, and the production of isomeric mesityloximes, therefore, cannot be ascribed to the existence of isomeric ketones in the commercial product.

Pinner's compound melts at  $95^\circ$  and becomes anhydrous in a vacuum over sulphuric acid, when it melts at  $158$ — $160^\circ$  without decomposing; regeneration of mesitylic oxide may be effected either by dry distillation, or through the agency of caustic soda.

M. O. F.

**Stereoisomeric Mesityloximes.** By CARL D. HARRIES and RICHARD GLEY (*Ber.*, 1899, 32, 1330—1338. Compare Harries and Jablonski, *Abstr.*, 1898, i, 401).—Although  $\alpha$ -mesityloxime is converted into the stable  $\beta$ -modification under the influence of acids, it is regenerated from this form by alkalis. The  $\alpha$ -oxime is therefore alkali-stable, and the  $\beta$ -oxime acid-stable, as represented by the

expressions,  $\ominus \text{CMe}_2 \cdot \text{CH} \cdot \underset{\text{N} \cdot \text{OH}}{\underset{|}{\text{C}}} \text{Me} \oplus$  and  $\ominus \text{CMe}_2 \cdot \text{CH} \cdot \underset{\oplus \text{OH} \cdot \text{N}}{\underset{|}{\text{C}}} \text{Me} \oplus$ ,

respectively (compare Abegg, this vol., i, 327).

Phosphorus pentachloride acts vigorously on the oximes, which become charred, and yield only small quantities of basic products. When the hydrochlorides are treated with boiling water, diacetone-hydroxylamine is produced. A boiling, concentrated solution of caustic potash resolves the  $\alpha$ -oxime into acetone and acetoxime. The following derivatives of the isomeric oximes have been prepared:

The *sodium* derivative of the  $\alpha$ -modification is a hygroscopic, crystalline mass, which decomposes at high temperatures without previous fusion; the *hydrobromide* sinters at  $93^\circ$ , and melts indefinitely at  $114^\circ$ . The *acetyl* derivative boils at  $104^\circ$  under 11 mm. pressure, and has a sp. gr. 0.9934 at  $14^\circ$ , and the *benzoyl* derivative crystallises from ether in colourless, four-sided plates melting at  $45$ — $46^\circ$ ; the phenylcarbimide compound crystallises from light petroleum in long needles and melts at  $82$ — $83^\circ$ . The *benzyllic ether* is a colourless,



highly refractive oil, which boils at  $131\text{--}132^\circ$  under 10—11 mm. pressure, and has a sp. gr. 0.9844 at  $16^\circ$ ; the *platinochloride* crystallises in needles.

The *sodium* derivative of the  $\beta$ -oxime is less hygroscopic than that of the isomeride; the *hydrobromide* forms white, four-sided plates which melt and decompose at  $129^\circ$ . The *acetyl* derivative boils at  $100^\circ$  under 8—9 mm. pressure, and has a sp. gr. 0.9945 at  $14^\circ$ ; it is hydrolysed much more readily by caustic soda than the isomeric modification. The *benzoyl* derivative crystallises from light petroleum in white prisms, melts at  $44\text{--}45^\circ$ , and forms an oil when mixed with the isomeride; the *phenylcarbimide compound* crystallises from light petroleum in four-sided plates, and melts at  $82\text{--}83^\circ$ . The *benzylic ether* is a colourless, highly refractive oil, which boils at  $129\text{--}130^\circ$  under 10 mm. pressure, and has a sp. gr. 0.9877 at  $16^\circ$ ; the *platinochloride* crystallises in beautiful, golden-yellow prisms. Concentrated hydrochloric acid resolves the benzylic ethers into benzylic chloride, ammonium chloride, benzoic acid, and a substance which reduces Fehling's solution.

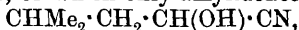
*Mesitylnitrimine*,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{N}\cdot\text{NO}_2$ , prepared by adding isomeric nitrite to a cooled solution of the  $\alpha$ -oxime in glacial acetic acid, crystallises from absolute alcohol in beautiful, white needles, and melts at  $155\text{--}156^\circ$ , when it decomposes vigorously; the  $\beta$ -oxime is indifferent to this treatment until heated on the water-bath, when the nitrimine is formed. The compound,  $\text{C}_6\text{H}_{10}\text{N}_2\text{Cl}_2\text{O}$ , obtained by heating the nitrimine with 40 per cent. hydrochloric acid on the water-bath, crystallises in lustrous leaflets and melts at  $48^\circ$ ; it is a remarkably stable substance, and resists the action of concentrated sulphuric and nitric acids at  $120^\circ$ .  
M. O. F.

**Hydroxynitriles containing Five and Six Carbon Atoms.**  
By LOUIS HENRY (*Chem. Centr.*, 1899, i, 194—195; from *Bull. Acad. roy. Belg.*, [iii], 36, 241—262).—(1) *Derivatives containing  $\text{C}_5$* .—From the three pentanes, 12 hydroxynitriles are theoretically possible, but only 3 have been prepared. A fourth,  $\text{CN}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$ , is only known in the form of the corresponding ketone. *Normal butyldenecyanhydrin*,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CN}$ , prepared from but-aldehyde in the same way as that given for isobutyldenecyanhydrin (this vol., i, 255), is a thin, colourless liquid with a pleasant odour, and has a sp. gr. 0.9367 at  $24^\circ$ . When treated with phosphorus pentachloride, it forms  *$\alpha$ -chlorovaleronitrile*,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CN}$ , which is a thin, colourless liquid with a pleasant odour, boils at  $160^\circ$  under 764 mm. pressure, has a sp. gr. 0.9995 at  $24^\circ$ , and by the action of hydrochloric acid is converted into  $\alpha$ -chlorovaleric acid. *Methylic  $\alpha$ -chlorovalerate* boils at  $160^\circ$  under 764 mm. pressure.  *$\gamma$ -Methylcrotononitrile* or  *$\beta$ -ethylacrylonitrile*,  $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CN}$ , obtained by distilling normal butyldenecyanhydrin over phosphoric anhydride, is a colourless liquid, boils at  $140^\circ$  under 762 mm. pressure, and has a sp. gr. 0.8239 at  $24^\circ$ . The boiling points of the homologues of crotononitriles show a difference of  $20^\circ$ .

*Cyanobutylic acetate*,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CN}$ , prepared by the action of acetic chloride on butyldenecyanhydrin, is a limpid,

colourless liquid, boils at  $194^{\circ}$  under 762 mm. pressure, and has a sp. gr. 0.9696 at  $24^{\circ}$ . With dimethylamine, butyridenecyanhydrin forms a compound,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}(\text{NMe}_2)\cdot\text{CN}$ , which boils at  $175\text{--}176^{\circ}$ . *Methylethylglycollonitrile* (*methylethylketocyanhydrin*),  $\text{OH}\cdot\text{CMeEt}\cdot\text{CN}$ , prepared by the action of hydrocyanic acid on methyl ethyl ketone, is a thin, colourless liquid, boils at  $180^{\circ}$  under 762 mm. pressure, and has a sp. gr. 0.9212 at  $24^{\circ}$ ; the *acetate*,  $\text{OAc}\cdot\text{CMeEt}\cdot\text{CN}$ , is a thin, colourless liquid, boils at  $195^{\circ}$  under 764 mm. pressure, and has a sp. gr. 0.9629 at  $24^{\circ}$ . By the action of concentrated hydrochloric acid on the acetate, hydroxyvaleric acid is obtained, and by the action of phosphoric anhydride,  $\alpha$ -*methylcrotononitrile*,  $\text{CHMe}\cdot\text{CMe}\cdot\text{CN}$ . The latter is a thin, colourless liquid, boils at  $124\text{--}125^{\circ}$  under 767 mm. pressure, and has a sp. gr. 0.8143 at  $24^{\circ}$ ; its *dimethylamine* derivative,  $\text{NMe}_2\cdot\text{CMeEt}\cdot\text{CN}$ , boils at  $171^{\circ}$ . Tables are given showing the influence of the substitution of a hydrogen atom by a methyl group on the boiling points of saturated and unsaturated nitriles. All these compounds are insoluble in water, but dissolve in alcohol or ether.

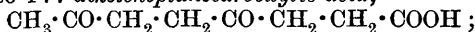
(2) *Derivatives containing C<sub>6</sub>*.—From hexane, 31 hydroxynitriles are theoretically possible, of which only amyridenecyanhydrin,



has hitherto been prepared. *Diethylketocyanhydrin* (*diethylglycollonitrile*),  $\text{OH}\cdot\text{CEt}_2\cdot\text{CN}$ , is a liquid, boils at  $184^{\circ}$ , and has a sp. gr. 0.9326 at  $22^{\circ}$ ; the *acetate* boils at  $212^{\circ}$  under 762 mm. pressure, and has a sp. gr. 0.9612 at  $22^{\circ}$ .  $\alpha$ -*Ethylcrotononitrile*,  $\text{CHMe}\cdot\text{CEt}\cdot\text{CN}$ , prepared by distilling the acetate over phosphoric anhydride, or by distilling the chloride, obtained by means of phosphorus pentachloride, over potassium hydroxide, is a colourless liquid, boils at  $143\text{--}145^{\circ}$ , and has a sp. gr. 0.8343 at  $22^{\circ}$ ; its *dimethylamine* derivative boils at  $176\text{--}177^{\circ}$  under 764 mm. pressure. *Methylisopropylketocyanhydrin* (*methylisopropylglycollonitrile*),  $\text{CHMe}\cdot\text{CMe}(\text{OH})\cdot\text{CN}$ , boils at  $182^{\circ}$  under 764 mm. pressure, and has a sp. gr. 0.9249 at  $18^{\circ}$ ; by the action of phosphoric anhydride, or by distilling the chloride, obtained by the action of phosphorus pentachloride, over potassium hydroxide, *trimethylacrylonitrile*,  $\text{CMe}_2\cdot\text{CMe}\cdot\text{CN}$ , is obtained as a colourless liquid which boils at  $155\text{--}157^{\circ}$ , and has a sp. gr. 0.8447 at  $18^{\circ}$ . The *acetate*,  $\text{CHMe}_2\cdot\text{C}(\text{OAc})\text{Me}\cdot\text{CN}$ , is a colourless liquid, boils at  $212^{\circ}$  under 764 mm. pressure, and has a sp. gr. 0.9750 at  $18^{\circ}$ . The *dimethylamine* derivative boils at  $176\text{--}177^{\circ}$ .

In the original paper, tables comparing the boiling points of the saturated and unsaturated nitriles are given. E. W. W.

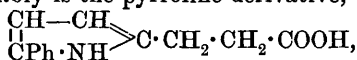
**Preparation of Monobasic 4:7-Diketonic Acids.** By EDUARD ALEXANDRE KEHRER and P. IGLER (*Ber.*, 1899, 32, 1176—1180).—By the action of alcoholic hydrogen chloride, furfurylideneacetone is converted into 4:7-diketoheptanecarboxylic acid,



this crystallises from ether in colourless, glistening, six-sided tablets, and melts at  $75\text{--}76^{\circ}$ ; it dissolves readily in water, chloroform, acetone, or alcohol, less readily in cold ether or benzene, and only slightly in light petroleum. The acid yields iodoform when treated

with iodine and caustic potash, gives a brilliant silver mirror with cold ammoniacal silver nitrate, reduces Fehling's solution on warming, and is rapidly oxidised by cold alkaline potassium permanganate. Concentrated sulphuric acid gives the crystals a reddish-yellow colour, and yields a yellow solution, which becomes deep red on exposure to air or on adding a little water, and turns violet on adding concentrated caustic potash solution. On warming with concentrated ammonium acetate, the pine-splinter reaction characteristic of pyrroline derivatives can be obtained, proving the acid to be a 4:7-diketone (Knorr, Abstr., 1886, 331).

*Phenyl-4:7-diketohexanecarboxylic acid*,  $\text{COPh} \cdot \text{C}_2\text{H}_4 \cdot \text{CO} \cdot \text{C}_2\text{H}_4 \cdot \text{COOH}$  (*phenacyllævulinic acid*), produced in a similar way from furfurylidene-acetophenone, melts at  $115-116^\circ$ , and is insoluble in water, but in other respects closely resembles the preceding acid; Knorr's test gives a violet and not a red coloration with a pine-splinter. On heating with ammonium acetate and acetic acid, a clear red solution is produced, with a strong violet-blue fluorescence; on diluting the solution with water, small, brown crystals separate, which also show a blue fluorescence; this probably is the pyrroline derivative,



corresponding with the diketonic acid (compare Kapff and Paul, Abstr., 1888, 840).

The two acids can also be prepared by the action of ethylic bromolævulinate on the sodium derivatives of ethylic acetate and benzoate.

T. M. L.

#### Catalytic Action of Metals on Solutions of Oxalic Acid.

By OTTOCAR ŠULC (*Zeit. physikal. Chem.*, 1899, 28, 719-722).—It has been observed by Jorissen that dilute solutions of oxalic acid decompose in the dark in the presence of moulds, and the author has observed that various metals produce a similar effect. The experimental numbers given show that palladium, platinum, and silver all cause, in the dark, a decrease of the strength of an *N*/10 oxalic acid solution, the effect being most marked for palladium.

L. M. J.

**Action of Inorganic Acidic Metallic Oxides on Organic Acids.** By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1899, 20, 281-322. See also Abstr., 1893, i, 626; 1896, i, 278 and 348).—I. *Uranyl-oxalates* [with HERMANN LIENAU].—Aqueous solutions of normal alkali oxalates dissolve only a small quantity of uranium trioxide; ammonium oxalate is an exception, and on boiling with uranium trioxide, ammonia is evolved until ammonium hydrogen oxalate is formed, and the reaction then proceeds as described below. Alkali hydrogen oxalate solutions, however, at their boiling temperatures, dissolve a considerable quantity of uranium trioxide, deep yellow solutions being obtained which, when concentrated on the water-bath, deposit the yellow, crystalline double salts. *Potassium uranyl oxalate*,  $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot 3\text{C}_2\text{O}_3 + 4\text{H}_2\text{O}$ , crystallises in lustrous, yellow, monoclinic crystals. The mother liquors, on further concentration, yield the salt  $\text{K}_2\text{O} \cdot \text{UO}_3 \cdot 2\text{C}_2\text{O}_3 + 3\frac{1}{2}\text{H}_2\text{O}$ , which crystallises in bright yellow crusts. This salt has been obtained by Ebelman by saturating a solution of uranium oxalate with potassium

hydrogen oxalate, but the authors were only able to obtain the first salt by this method. The *sodium* salt,  $\text{Na}_2\text{O}, \text{UO}_3, 2\text{C}_2\text{O}_3 + 4\text{H}_2\text{O}$ , crystallises in thin, lustrous plates, and can be recrystallised without decomposition. The *ammonium* salt,  $(\text{NH}_4)_2\text{O}, \text{UO}_3, 2\text{C}_2\text{O}_3 + 2\text{H}_2\text{O}$ , crystallises in large, yellow, transparent, monoclinic crystals. The *cæsium* salt,  $\text{Cs}_2\text{O}, 2\text{UO}_3, 3\text{C}_2\text{O}_3$ , crystallises in small, yellowish-green tablets, and is insoluble both in cold and in boiling water. The authors were unable to obtain a *cæsium* salt corresponding in composition with the sodium salt. The *lithium* salt,  $\text{Li}_2\text{O}, \text{UO}_3, 2\text{C}_2\text{O}_3 + 4\frac{1}{2}\text{H}_2\text{O}$ , crystallises in large, monoclinic crystals, and is obtained mixed with a basic uranium oxalate of the composition  $2\text{UO}_3, \text{C}_2\text{O}_3 + 7\text{H}_2\text{O}$ . The alkali uranyloxalates of the composition  $\text{R}_2\text{O}, \text{UO}_3, 2\text{C}_2\text{O}_3$  are decomposed when treated with chlorides of the alkaline earths; with calcium and strontium chlorides, the solution remains clear for 12 hours in the cold, but for not more than half an hour on heating, although a part only of the oxalic acid is precipitated. With barium chloride, a magma is obtained consisting of slender, yellowish-white needles of the salt  $3(\text{BaO}, \text{UO}_3, 2\text{C}_2\text{O}_3, 10\text{H}_2\text{O}), \text{BaC}_2\text{O}_4$ , mixed with barium oxalate; on heating, the double salt decomposes into barium oxalate. A determination of the conductivity of solutions of the sodium salt gives results closely approaching the value for a normal salt of a dibasic acid.

II. Compounds of antimony trioxide and bismuth oxide. [With KARL BIERBRAUER.]—Antimony oxalate,  $\text{Sb}_2\text{O}_3, 2\text{C}_2\text{O}_3 + 1\frac{1}{2}\text{H}_2\text{O}$ , obtained by precipitating a solution of antimony trioxide in tartaric acid with a concentrated solution of oxalic acid, is a white precipitate of microscopic needles. A salt of the composition  $2\text{Sb}_2\text{O}_3, 5\text{C}_2\text{O}_3 + 7\text{H}_2\text{O}$  is obtained by heating freshly precipitated antimony oxide with oxalic acid under pressure; it crystallises in needles, is unstable, and cannot be obtained pure. The alkali antimonyl oxalates,  $3\text{R}_2\text{O}, \text{Sb}_2\text{O}_3, 6\text{C}_2\text{O}_3$ , correspond with the more stable compounds derived from the sesquioxides of aluminium, iron, and chromium. The *potassium* salt, with  $8\text{H}_2\text{O}$ , is obtained by gradually adding freshly precipitated antimony trioxide to a boiling solution of potassium hydrogen oxalate, and as soon as the solution is saturated, filtering through a hot water filter. If the solution is boiled after saturation, decomposition takes place; it crystallises in aggregates of needles, dissolves without decomposition in cold water, and then gradually decomposes, with precipitation of antimonious acid. When treated with a few drops of strong mineral acid, the solution at once deposits the salt  $\text{Sb}_2\text{O}_3, 2\text{C}_2\text{O}_3 + 1\frac{1}{2}\text{H}_2\text{O}$ . This reaction points to the conclusion that it is a salt of the complex acid  $\text{Sb}(\text{COO}-\text{COOH})_3$ , which is not stable, but at once decomposes into antimony oxalate. The *sodium* salt, with  $10\text{H}_2\text{O}$ , is very unstable and difficult to prepare; it is obtained by saturating a solution of sodium hydrogen oxalate with antimony trioxide at the temperature of the water-bath, and then fractionally crystallising the solution, when it is obtained in the third fraction in the form of small, rhombic crystals mixed with monoclinic prisms of the sodium salt. The *ammonium* salt, with  $3\text{H}_2\text{O}$ , is obtained by precipitating a solution of antimony trioxide in ammonium hydrogen oxalate with an equal bulk of alcohol, and after separating the precipitate, adding three volumes of alcohol to the filtrate, when it crystallises in small, lustrous needles.

*Alkali antimonyloxalates*,  $5\text{R}_2\text{O}, 2\text{Sb}_2\text{O}_3, 11\text{C}_2\text{O}_3$ . The *potassium* salt, with 28 or  $7\text{H}_2\text{O}$ , is obtained by partially decomposing the preceding potassium salt by boiling its aqueous solution; it crystallises in monoclinic prisms from the mother liquors, after the removal of any undecomposed salt, and decomposes when treated with cold water, with the separation of antimony oxide. The *sodium* salt,  $2\text{Na}_2\text{O}, \text{Sb}_2\text{O}_3, 4\text{C}_2\text{O}_3 + 5\text{H}_2\text{O}$ , crystallises in large, monoclinic prisms, and is decomposed by cold water with formation of antimony oxide; when treated with dilute sulphuric acid, it yields antimony oxalate, and gives all the reactions of antimony and oxalic acid. The *potassium* salt,  $\text{K}_2\text{O}, \text{Sb}_2\text{O}_3, 4\text{C}_2\text{O}_3 + 2\text{H}_2\text{O}$ , obtained by adding the theoretical quantity of oxalic acid to a concentrated solution of potassium antimonyl oxalate,  $\text{Sb}(\text{CO}_2 \cdot \text{CO}_2\text{K})_3 + 4\text{H}_2\text{O}$ , and boiling for a short time, crystallises in needles. The corresponding *ammonium* salt, with  $12\text{H}_2\text{O}$ , crystallises in beautiful, prismatic crystals. The two preceding salts differ from the normal antimonyl oxalates only in their instability when treated with water, when they are completely decomposed, with the formation of antimonious acid.

Besides the preceding compounds, a series of salts has been described which are double salts of the preceding antimonyloxalate with alkali hydrogen oxalate. The salt  $4(\text{NH}_4)_2\text{O}, \text{Sb}_2\text{O}_3, 8\text{C}_2\text{O}_3 + 11\text{H}_2\text{O}$ , obtained by saturating a boiling solution of ammonium hydrogen oxalate with antimony trioxide, crystallises in beautiful, rhombic tablets. The salt  $5\text{K}_2\text{O}, \text{Sb}_2\text{O}_3, 10\text{C}_2\text{O}_3 + 12\text{H}_2\text{O}$ , obtained from the last mother liquors in the preparation of normal potassium antimonyloxalate, separates in lustrous crystals, and dissolves without decomposition in cold water. The salt  $2(\text{NH}_4)_2\text{O}, \text{Sb}_2\text{O}_3, 6\text{C}_2\text{O}_3 + 6\text{H}_2\text{O}$  is obtained by the same method as the preceding ammonium salt.

The authors were unable to obtain complex or double salts of arsenious acid and oxalic acid.

*Bismuth oxalate*,  $\text{Bi}_2\text{O}_3, 3\text{C}_2\text{O}_3 + 7\frac{1}{2}\text{H}_2\text{O}$ , is obtained as a white, crystalline precipitate by adding a concentrated solution of oxalic acid to a solution of bismuth nitrate in dilute nitric acid. When bismuth hydroxide is boiled with a solution of oxalic acid, only a very small quantity of this salt is formed. A basic salt corresponding with antimony oxalate cannot be prepared. *Potassium bismuth oxalate*,  $\text{K}_2\text{C}_2\text{O}_4 + \text{Bi}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$ , obtained by warming concentrated solutions of potassium oxalate and bismuth oxalate on the water-bath, crystallises in beautiful, microscopic, radiating aggregates of prisms, is insoluble in cold water, but completely decomposed by hot water, and gives all the reactions of bismuth and oxalic acid; it cannot be prepared by boiling bismuth hydroxide with potassium hydrogen oxalate, and is therefore a double, and not a complex, salt. The *ammonium* salt,  $3(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{Bi}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$ , obtained in a similar manner to the potassium salt, crystallises in characteristic pyramids. The potassium and ammonium salts described by Souchay and Lenssen are mixtures of the preceding salts with 10 and 7 mols. of potassium oxalate, and 12 mols. of ammonium oxalate. The corresponding sodium compounds could not be prepared owing to the insolubility of sodium oxalate.

*Stannioxalates* [with MAX PLATSCH].—*Potassium stannioxalate*,

$3\text{K}_2\text{O}, 2\text{SnO}_2, 7\text{C}_2\text{O}_3 + 5\text{H}_2\text{O}$ , is obtained by dissolving freshly precipitated stannic hydroxide in a concentrated solution of potassium hydrogen oxalate. The solution, on cooling, deposits a large quantity of colloidal stannic acid, which is separated, and the clear filtrate yields the salt in white, monoclinic crystals; it gives a clear solution in water, can be recrystallised without decomposition, and does not give the ordinary reactions for tin or oxalic acid. The corresponding sodium and ammonium salts cannot be prepared. The acid oxalates freely dissolve stannic hydroxide, but on concentration of the clear filtrate decomposition occurs, and stannic acid and alkali hydrogen oxalate are formed. The *barium* salt,  $2\text{BaO}, \text{SnO}_2, 4\text{C}_2\text{O}_3 + 8\text{H}_2\text{O}$ , obtained by adding barium chloride to a solution of the potassium salt, crystallises in white needles and is insoluble. When the potassium salt is treated with calcium, strontium, or nickel chloride, stannic acid and the metallic oxalate are formed. The free stannioxalic acid cannot be isolated; the amorphous compound obtained by dissolving stannic hydroxide in oxalic acid, or by decomposing the barium salt with sulphuric acid, is colloidal stannic acid mixed with oxalic acid; the latter can be washed out by treatment with water.

The above results confirm the authors' views. The formation of complex acids depends on the relative affinities of their components; the acids formed are stronger and more capable of forming salts according as more hydroxyl groups of the sesquioxide are replaced by oxalic acid groups, and as the sesquioxide becomes less basic in character.

E. C. R.

**Complex Platinum Salts: Oxalates and Chlorides.** By MAURICE VEZES (*Bull. Soc. Chim.*, 1898, [iii], 19, 875—879).—When excess of normal potassium oxalate is added to a hot, concentrated solution of potassium platosochloride, the liquid, originally dark red, becomes much paler, and, on cooling, deposits straw-yellow, optically active prismatic crystals of Söderbaum's platoso-oxalate,  $\text{Pt}(\text{C}_2\text{O}_4)_2\text{K}_2 + 2\text{H}_2\text{O}$ . This reaction, in which the platoso-chloride is directly converted into the corresponding platoso-oxalate, affords a simpler and more convenient means of preparing the latter than the indirect methods hitherto employed (see Abstr., 1896, i, 465). The converse transformation of platoso-oxalate into platoso-chloride is readily effected by the action of hydrochloric acid. The platoso-oxalate may also be prepared from potassium platinochloride by boiling a concentrated solution of this salt with excess of potassium oxalate (3 mols.). In this reaction, one-third of the potassium oxalate employed is used in the reduction of the platinochloride to the platoso-chloride, with evolution of carbonic anhydride.

N. L.

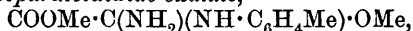
**Action of Ammonia and Substituted Ammonias on Methylic Dichloroxalate and on Methylic Semiorthoxalate: Diamido-esters.** By RICHARD ANSCHÜTZ and JULIUS STIEPEL (*Annalen*, 1899, 306, 5—27. Compare Abstr., 1895, i, 170).—The action of dried ammonia on methylic dichloroxalate yields the hydrochloride of methylic diamido-oxalate,  $\text{COOMe}\cdot\text{C}(\text{NH}_2)_2\cdot\text{OMe}$ , which spontaneously changes into ammonium chloride and methylic imido-oxalate,  $\text{COOMe}\cdot\text{C}(\text{NH})\cdot\text{OMe}$ ; methylic alcohol converts both substances into

methylic semi-orthoxalate,  $\text{COOMe}\cdot\text{C}(\text{OMe})_3$ . *Dimethylic diethylic semi-orthoxalate*,  $\text{COOMe}\cdot\text{C}(\text{OEt})_2\cdot\text{OMe}$ , obtained by the action of ammonia on a solution of methylic dichloroxalate in a mixture of ether and ethylic alcohol, is a colourless liquid which boils at  $89^\circ$  under 12 mm. pressure.

*Methylic diparatoluidido-oxalate*,  $\text{COOMe}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2\cdot\text{OMe}$ , prepared from paratoluidine and methylic dichloroxalate, crystallises from ether and melts at  $105^\circ$ ; it forms a *platinochloride*. *Methylic semiparatolylimido-oxalate*,  $\text{COOMe}\cdot\text{C}(\text{OMe})\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ , produced when the action takes place in hot xylene, separates from alcohol in pale yellow crystals and melts at  $145^\circ$ .

*Methylic semiphenylhydrazono-oxalate*,  $\text{COOMe}\cdot\text{C}(\text{OMe})\cdot\text{N}\cdot\text{NHPH}$ , obtained from phenylhydrazine and methylic dichloroxalate in cold ether, separates from alcohol in pale yellow, well-formed crystals and melts at  $126^\circ$ ; concentrated sulphuric acid develops a blue coloration. The compound  $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_4$  or  $\text{C}_6\text{H}_9\text{N}_3\text{O}_3$ , produced when methylic semi-orthoxalate is heated with acetamide, crystallises from a mixture of alcohol and ether in colourless, hygroscopic needles. Diphenylamidinoxanilide (*loc. cit.*) belongs to the triclinic system [ $a:b:c = 0.3759:1:0.3772$ ;  $\alpha = 94^\circ 32'$ ,  $\beta = 91^\circ 10'$ ,  $\gamma = 63^\circ 5'$ ]. Diparatolyl amidinoxaloparatoluidide is also triclinic [ $a:b:c = 0.9840:1:0.5723$ ;  $\alpha = 98^\circ 48'$ ,  $\beta = 99^\circ 26'$ ,  $\gamma = 86^\circ 40'$ ].

*Methylic amidoparatoluidido-oxalate*,



prepared from ammonia and methylic semiparatoluido-oxalate, is a white powder which melts at  $236^\circ$ . M. O. F.

**$\beta\beta$ -Dimethylglutaric Acid.** By GUSTAV KOMPPA (*Ber.*, 1899, 32, 1421—1424).—This acid (Auwers, *Abstr.*, 1895, i, 410; W. H. Perkin, jun., *Trans.*, 1896, 1474; 1899, 48) is best prepared in the following manner. Sodium is dissolved in alcohol, the solution when cold is mixed with ethylic malonate and then with mesitylic oxide, being shaken meanwhile, after which it is boiled for 45 minutes in a reflux apparatus. The hot mixture is then poured into a hot solution of barium hydroxide in water, the whole boiled for 20 hours in a large vessel, made slightly acid with hydrochloric acid, filtered if necessary, concentrated, mixed with a large excess of hydrochloric acid, boiled for a short time, and then allowed to cool; dimethylhydroresorcinol then crystallises out (compare Vorländer, *Abstr.*, 1897, i, 276). This is boiled for 5 minutes with a solution of potassium hydroxide in water, cooled, and added gradually to a solution made by pouring water over bromine, cooling the mixture with snow, shaking, and adding aqueous caustic soda gradually until the bromine has dissolved and the colour due to it has disappeared. The whole is allowed to remain until a portion gives no precipitate with hydrochloric acid, mixed with excess of sodium sulphite, filtered, and the solution made strongly acid with hydrochloric acid, concentrated to half its volume, and extracted with ether; upon evaporation of the extract,  $\beta\beta$ -dimethylglutaric acid remains in almost quantitative yield. The *dimethylic* salt boils at  $103$ — $104^\circ$  under 15 mm. pressure,

and has a sp. gr. 1.0385 at 20°/20°; the diethylic salt, in the same circumstances, boils at 127—128°, and has a sp. gr. 0.9929.

If the mixture with the hypobromite is allowed to remain only a short time, *bromodimethylhydroresorcinol*,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} \text{CHBr}$ , separates when the acid is added; this melts at 173—174°, and is converted into  $\beta\beta$ -dimethylglutaric acid by further treatment with hypobromite. C. F. B.

**Preparation of Hydroxysuccinic Acid ( $\alpha$ -Isomalic Acid) from Pyruvic Acid.** By HERBERT POMMEREHNE (*Arch. Pharm.*, 1899, 237, 161—170).—Schmöger first obtained this acid,  $\text{OH} \cdot \text{CMe}(\text{COOH})_2$ , by the action of moist silver oxide on monobromisuccinic acid. Then Böttiger, by adding hydrogen cyanide to pyruvic acid and hydrolysing the product with baryta, obtained a "methyldtartronic acid," which should have been identical with Schmöger's acid, but was, in fact, found to be different. Later observations by other chemists have confirmed the discrepancy without explaining it.

The author finds that if the hard cake, which is formed as the crude product when pyruvic acid is added to powdered potassium cyanide, is moistened with fuming hydrochloric acid, and then boiled with strong hydrochloric acid for  $\frac{1}{2}$ — $\frac{3}{4}$  hour,  $\alpha$ -isomalic acid is obtained melting and decomposing at 141°, and convertible into ethylidenelactic acid by heating at 145°. The result is the same if the compound  $\text{OH} \cdot \text{CMe}(\text{CN}) \cdot \text{COOK} + \text{C}_2\text{H}_5 \cdot \text{OH}$ , obtained by adding pyruvic acid to potassium cyanide suspended in boiling alcohol, is treated in the same manner. But when  $7\frac{1}{2}$  per cent. baryta water is used instead of hydrochloric acid, the boiling being continued until no more ammonia is evolved, the product in both cases is Böttiger's acid; this melts at 101—103° when dried in the air, and decomposes at 170—180° when dried over sulphuric acid or at 182—185° when dried at 60—70°. The hydrolysis evidently takes an abnormal course when baryta is the agent employed; the nature of the acid formed is undergoing investigation. C. F. B.

**Action of Carbamide on Ethylic Dioxysuccinate.** By HANS GEISENHEIMER and RICHARD ANSCHÜTZ (*Annalen*, 1899, 306, 38—71).—Although carbamide suffers condensation with glyoxal, diacetyl, benzil,  $\beta$ -naphthaquinone, and phenanthraquinone, it yields an additive compound with ethylic dioxysuccinate (compare Abstr., 1895, i, 172).

Ethylic dihydroxysuccinate *ureine*,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{COOEt} \\ \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{COOEt} \end{smallmatrix}$  prepared by heating ethylic dioxysuccinate with a solution of carbamide in glacial acetic acid, has no definite melting point, but decomposes and evolves gas at 164—165°; it separates from water in rhombic crystals [ $a:b:c = 0.77068:1:3.30967$ ]. The ureine is neutral, and is indifferent towards phenylhydrazine; hot caustic soda eliminates ammonia, and alcoholic hydrochloric acid at 100° converts it into the diureine described by Anschütz and Geldermann (Abstr., 1891, 725). The



ureine of ethylic diacetoxysuccinate,  $C_3N_2H_2O(OAc)_2(COOEt)_2$ , obtained on heating the foregoing substance with acetic acid and acetic chloride, melts at  $158-159^\circ$ ; boiling water eliminates the acetyl groups.

The *ureine* of dihydroxysuccinamide,  $CO \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{CONH}_2 \\ | \\ \text{NH} \cdot \text{C}(\text{OH}) \cdot \text{CONH}_2 \end{smallmatrix}$ , produced when ammonia is passed into an alcoholic solution of the ureine, decomposes and evolves gas at  $179^\circ$ .

The *ureine* of ethylic diethoxysuccinate,  $C_3N_2H_2O(OEt)_2(COOEt)_2$ , is formed when carbamide acts on ethylic dioxysuccinate under the influence of alcoholic hydrogen chloride, provided the temperature is not maintained at the boiling point during a long period, in which case the diureine is produced; it crystallises from alcohol and from hot water in slender needles, and decomposes at  $187-188^\circ$ . The *ureine* of diamidosuccinamide,  $CO \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{CONH}_2 \\ | \\ \text{NH} \cdot \text{C}(\text{NH}_2) \cdot \text{CONH}_2 \end{smallmatrix}$ , obtained by the action of alcoholic ammonia, does not melt below  $290^\circ$ .

The *compound*  $C_9H_{12}N_2O_5$ , produced by treating the ureines of ethylic dioxysuccinate and of ethylic diethoxysuccinate with phosphorus trichloride, crystallises from acetone in aggregates of needles, and melts at  $200^\circ$ ; its constitution is probably expressed by one of the formulæ  $CO \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{COOEt} \\ | \\ \text{NH} \cdot \text{C} \cdot \text{COOEt} \end{smallmatrix}$  and  $CO \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{COOEt} \\ | \\ \text{N} = \text{C} \cdot \text{COOEt} \end{smallmatrix}$ .

The diureine of ethylic succinate already described by Anschütz and Geldermann (*loc. cit.*) becomes yellow at  $220^\circ$  and decomposes at  $272^\circ$ .

The *diureine* of succinic acid,  $CO \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{COOH}) \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{C}(\text{COOH}) \cdot \text{NH} \end{smallmatrix} > CO$ , decomposes and evolves gas at  $183-184^\circ$ ; the *ammonium* salt, obtained by the action of ammonium carbonate on the diureine of ethylic dioxysuccinate, forms small, rhombic crystals containing  $1H_2O$ , and the *silver* salt is anhydrous.

Methylic dihydroxysuccinate *ureine*,  $C_3N_2H_2O(OH)_2(COOEt)_2$ , melts and evolves gas at  $179-180^\circ$ ; it separates from alcohol in transparent, colourless crystals belonging to the rhombic system [ $a:b:c = 0.7386:1:3.0499$ ]. The *ureine* of methylic dimethoxysuccinate,

$CO \begin{smallmatrix} \text{NH} \cdot \text{C}(\text{OMe}) \cdot \text{COOMe} \\ | \\ \text{NH} \cdot \text{C}(\text{OMe}) \cdot \text{COOMe} \end{smallmatrix}$ , melts and decomposes at  $200-201^\circ$ . The *diureine* of methylic succinate crystallises from hot water in small needles, and decomposes at  $280^\circ$ , evolving gas.

Ethylic succinate *methyl*diureine,  $CO \begin{smallmatrix} \text{NMe} \cdot \text{C}(\text{COOEt}) \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{C}(\text{COOEt}) \cdot \text{NH} \end{smallmatrix} > CO$ , prepared by heating methylcarbamide and ethylic diethoxysuccinate with alcoholic hydrogen chloride at  $100^\circ$ , crystallises from hot water in small needles, and melts, evolving gas, at  $248-249^\circ$ .

The *thioureine* of ethylic dioxysuccinate, prepared by heating alcoholic thiocarbamide with ethylic dioxysuccinate in a reflux apparatus, becomes reddish-yellow at  $135^\circ$ , and melts at  $150-151^\circ$ , vigorously evolving gas; it crystallises from ethylic acetate in colourless, transparent crystals belonging to the rhombic system [ $a:b:c = 0.7376:1:3.2443$ ].

M. O. F.

**Lævorotation of Dextrotartaric Acid in Concentrated Aqueous Solution.** By N. LEPESCHKIN (*Ber.*, 1899, 32, 1180—1184).—The specific rotatory power of dextrotartaric acid decreases with decreasing temperature and with increasing concentration; for each wave-length there should therefore be a concentration beyond which the acid would be lævorotatory. This cannot be observed with saturated solutions, as the concentrations required lie beyond the limits of solubility, but with a supersaturated solution containing 66.48 per cent. of tartaric acid, the author has observed a lævorotation  $[\alpha]_D - 1.22^\circ$  for dark-blue light at  $20^\circ$ . With increasing wave-length, the solution becomes more and more dextrorotatory, but the dextrorotation reaches a maximum in the yellow part of the spectrum, and then decreases in the red, without, however, becoming zero again. At higher temperatures, the dextrorotatory power of the solution increases, and in spite of the increase of solubility it is not possible to obtain a lævorotatory solution. T. M. L.

**d-Trihydroxyglutaric Acid.** By EDMUND O. VON LIPPMANN (*Ber.*, 1899, 32, 1213).—The d-trihydroxyglutaric acid described by Ruff (this vol., i, 324) is identical with that previously obtained by the author by the action of dilute acids on sugar (*Abstr.*, 1894, i, 106). A. H.

**Preparation and Reduction of Dehydromucic Acid.** By HENRY B. HILL (*Ber.*, 1899, 32, 1221—1222).—[With ISAAC K. PHELPS.]—Dehydromucic acid can be conveniently prepared by boiling potassium hydrogen saccharate with hydrobromic acid under the ordinary pressure, the yield obtained in this way being equal to that obtained by the action of hydrochloric acid in sealed tubes.

[With A. S. WHEELER.]—On reduction, dehydromucic acid yields the two acids described by Seelig (*Ber.*, 1879, 12, 1082), which Schrötter (*Abstr.*, 1888, 1060) was unable to obtain. The acid of higher melting point is formed by the action of the alkali present on the isomeride. Both these acids yield with bromine the crystalline additive products  $C_6H_6Br_2O_5 \cdot H_2O$  melting at  $145^\circ$ , and  $C_6H_6Br_2O_5 \cdot 2H_2O$  melting at  $207^\circ$ . A. H.

**Action of Sodium on Ethylic Malonate.** By RICHARD WILLSTÄTTER (*Ber.*, 1899, 32, 1272—1285).—*Ethylic acetonedicarboxylate*,  $COOEt \cdot CH_2 \cdot CO \cdot CH(COOEt)_2$ , is obtained by the action of sodium on dry ethylic malonate under certain conditions, which are described in detail in the original. It is a colourless oil which boils at  $182$ — $183^\circ$  under 20 mm. pressure, and has a sp. gr.  $1.139$  at  $13^\circ/4^\circ$ . With ferric chloride, its alcoholic solution gives an intense cherry-red coloration; it is practically insoluble in water, but is miscible with most organic solvents, is soluble to a certain extent in dilute acids, and dissolves readily in alkalis, even in bicarbonate solutions, without the evolution of carbonic anhydride; its aqueous alcoholic solution reddens litmus, but cannot be titrated with litmus as indicator; it is volatile with steam, but at the same time undergoes decomposition, and reacts readily with bromine, potassium permanganate, or warm nitric acid. With semicarbazide, it yields a crystalline compound, which, however, has not the composition of the semicarbazone.

The *copper* salt of ethylic acetoneetricarboxylate,  $(C_{12}H_{17}O_7)_2Cu, 2H_2O$ , differs considerably from that of ethylic acetonedicarboxylate, and is useful in characterising the ethylic salt; it crystallises in small, silky, pale green, star-shaped needles, is insoluble in water or light petroleum, but dissolves very readily in methylic or ethylic alcohol, also in chloroform, benzene, and even ether. The hydrated salt melts at  $83-85^\circ$ , and the anhydrous at  $58-60^\circ$ . A *potassium* derivative of ethylic acetoneetricarboxylate,  $C_{12}H_{16}O_7K_2, KHCO_3$ , and *silver* salt,  $C_{12}H_{15}O_7Ag_3$ , have been obtained.

The distillate obtained during the preparation of the ethylic salt consists of ethylic acetate, alcohol, and a minute quantity of ethylic malonate. Among the other products formed is a yellow compound,  $C_{18}H_{18}O_{11}$ , which crystallises in long, pale yellow plates or short, cruciform needles melting at  $177-178^\circ$ .

The hydrolysis of the ethylic salt to the corresponding ketonic acid has not been accomplished, but both ketonic and acid hydrolysis readily take place. Ethylic phloroglucinoltricarboxylate (von Baeyer, Abstr., 1886, 223) is obtained when ethylic acetoneetricarboxylate and malonate, in molecular proportion, are warmed with pure ether and sodium ethoxide (3 mols.) free from alcohol; after a short time, the ether is distilled over, and the residue heated to  $145^\circ$ , then dissolved in water, and the clear solution saturated with carbonic anhydride, when ethylic phloroglucinoltricarboxylate is precipitated, the yield being about 50 per cent. of the theoretical. J. J. S.

**Derivatives of Aconitic Acid.** By D. C. HANNA and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 381—383).—On distilling sodium aconitate with twice its weight of phosphorus trisulphide, passing the evolved vapours into water, and distilling the aqueous solution with steam in presence of sodium hydroxide, small quantities of an oil passed over, which was identified as thiophthen (Abstr., 1886, 1032). A better yield is obtained if aconitic acid is used in place of its salt, but in this case the distillation with phosphorus trisulphide proceeds with great violence and large volumes of hydrogen sulphide are evolved.

The authors support Conen's view (Abstr., 1880, 36), that the action of phosphorus trichloride on triethylic citrate at  $100^\circ$  gives rise to triethylic aconitate. T. H. P.

**Synthesis of Methoxytricarballic Acid from Oxalic and Malonic Acids.** By RICHARD ANSCHÜTZ and THOMAS CLARKE (*Annalen*, 1899, 306, 28—38).—*Methylic aa-dicarboxymethoxytricarballic acid*,  $COOMe \cdot C[CH(COOMe)_2]_2 \cdot OMe$ , prepared by heating an ethereal solution of methylic dichloroxalate with methylic sodiomalonate (4 mols.) in a reflux apparatus, separates from alcohol in colourless crystals belonging to the triclinic system and melting at  $66^\circ$  [ $a:b:c = 0.5254:1:0.485$ ;  $\alpha = 101^\circ 57'$ ,  $\beta = 96^\circ 55'$ ,  $\gamma = 87^\circ 40\frac{1}{2}'$ ]. The *sodium* derivative is an orange-yellow, amorphous, deliquescent powder. The *acid*,  $COOH \cdot C[CH(COOH)_2]_2 \cdot OMe$ , separates from glacial acetic acid in very small crystals, and melts at  $180-185^\circ$ , evolving carbonic anhydride; the *silver* salt is insoluble in water, resisting the action of light, and the *barium* salt is anhydrous.

*Methoxytricarballic acid*,  $COOH \cdot C(CH_2 \cdot COOH)_2 \cdot OMe$ , obtained by

the action of concentrated alkali on dicarboxymethoxytricarballic acid, separates from glacial acetic acid in small, well-formed crystals, and melts with decomposition at 176—178°; the *silver* and *barium* salts are amorphous, whilst the *calcium* salt forms a white, crystalline powder. The *methylic* salt is a colourless liquid which boils at 163° under 12 mm. pressure.

*Methylic aa-dimethyl-aa-dicarboxymethoxytricarballylate*,  
 $\text{COOMe} \cdot \text{C}[\text{CMe}(\text{COOMe})_2]_2 \cdot \text{OMe}$ ,

prepared by heating the disodium derivative of methylic *aa*-dicarboxymethoxytricarballylate with methylic iodide in sealed tubes at 100°, separates from methylic alcohol in beautiful, transparent crystals, and melts at 100°.

M. O. F.

**Furfurylic Alcohol.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1899, 128, 1035—1038).—Pure furfurylic alcohol prepared by the action of concentrated sodium hydroxide solution on furfuraldehyde (*Abstr.*, 1893, i, 311) boils at 74—74·5° under 17 mm. pressure and at 168·5—169·5° under 752 mm. pressure. Its heat of combustion is 612·5 Cal. at constant volume and 612·78 Cal. at constant pressure and its heat of formation from its elements is +65·72 Cal. The differences between the alcohol and aldehyde +16·02 Cal. and the alcohol and acid 49·68 Cal. are of the same order of magnitude as in the case of benzylic and amylic alcohols and their corresponding derivatives.

The conversion of arabitol into furfurylic alcohol, like that of arabinose into furfuraldehyde, practically does not give rise to any thermal disturbance.

The heat of dissolution of furfurylic alcohol in water is +0·715 Cal. at about 13°. Its mean specific heat between 14° and 90° is 0·505 and its molecular heat 49·5 Cal., which is 11 Cal. higher than the molecular heat of furfuraldehyde.

C. H. B.

**Reactions of Unsaturated Ketones.** By CARL D. HARRIES (*Ber.*, 1899, 32, 1315—1320).—A theoretical discussion of the experimental results obtained by the author and his collaborators (following abstract and this vol., i, 566, 583, 624, 629, 637).

M. O. F.

**Reduction of  $\alpha\beta$ -Unsaturated Ketones.** By CARL D. HARRIES and FRIEDRICH KAISER (*Ber.*, 1899, 32, 1320—1326. Compare Harries and Eschenbach, *Abstr.*, 1896, i, 305).— $\alpha$ -Furfurylbutanone,  $\text{C}_4\text{OH}_8 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$ , representing 40 per cent. of the product obtained by reducing furfurylideneacetone with sodium amalgam and glacial acetic acid, forms a colourless oil with an agreeable, fruity odour, boils at 203° under atmospheric pressure, and at 101—102° under 22 mm., and has a sp. gr. 1·0361 at 19°/4°. The sodium hydrogen sulphite compound forms lustrous, colourless leaflets, and the semicarbazone melts at 143°; the parabromophenylhydrazone crystallises in flattened, golden-yellow prisms, and melts at 103—104°.

4 : 5-Di- $\alpha$ -furfuryloctanedione-2 : 7,  $\text{C}_8\text{H}_{12}(\text{C}_4\text{OH}_8)_2(\text{CH}_2 \cdot \text{COMe})_2$ , also obtained by reducing furfurylideneacetone, crystallises from benzene in elongated, transparent prisms, and melts at 123—124°; the diphenylhydrazone melts to a brown liquid at 181—183°.

Diketodimethyldihexahydrophenyl, obtained by reducing methyl-

cyclohexenone with alcohol and sodium amalgam (Abstr., 1898, i, 582), yields the *diphenylhydrazone* in leaflets melting at 210° when slowly heated, and at 213—215° when the temperature rises rapidly; the semi-carbazone melts and decomposes at about 248—250°.

3:5-Dimethyl- $\Delta^2$ -cyclohexenone yields *diketotetramethyldihexahydrophenyl*,  $C_2Me_2\left(\begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{CHMe} \end{array} \text{CH}_2\right)_2$ , which crystallises in prismatic plates and melts at 175° (compare Knoevenagel, this vol., i, 340); the *parabromophenylhydrazone* melts at 215—220°.

Wallach and Löhr have reduced carvone with zinc dust and caustic soda, obtaining dihydrocarvone and carvelone (this vol., i, 530); if, however, the reduction is effected with sodium amalgam in dilute acetic acid, bimolecular products are obtained in quantitative amount. Dicarvelone prepared in this manner melts at 148—149°, and appears to be identical with the compound described by Wallach and Löhr, but whilst the diphenylhydrazone obtained by these authors melts at 215°, that prepared by Harries and Kaiser melts at 268° when slowly heated, and at 271° when the temperature rises rapidly.

*Dicarvelol*,  $C_{20}H_{32}(OH)_2$ , obtained by reducing dicarvelone with sodium in absolute alcohol, sinters at 171—172°, and melts at 185°, a specimen having been obtained on one occasion melting at 203—205°; the *dihydrobromide* melts at 226°.

*Biscarvene*,  $C_2H_2\left[\begin{array}{c} \text{CMe} \text{---} \text{CH} \\ \text{CH}_2 \cdot \text{CH}(\cdot\text{CMe};\text{CH}_2) \end{array} \text{CH}_2\right]_2$ , is the name which the authors prefer for the hydrocarbon,  $C_{20}H_{30}$ , obtained by the action of phosphoric anhydride on dicarvelol; it is a pale yellow liquid having the odour of caoutchouc, and boils at 169—171° under 11 mm. pressure. When a solution of bromine in glacial acetic acid is added to biscarvene in the same medium, bromine is absorbed, and a dark violet coloration produced; concentrated sulphuric acid develops a deep red coloration with the hydrocarbon.

M. O. F.

### Trimethylene Mercaptan and the Trimethylenedisulphones.

By WILHELM AUTENRIETH and K. WOLFF (*Ber.*, 1899, 32, 1368—1375). —Trimethylene mercaptan can be readily prepared by the action of alcoholic potassium hydrosulphide on trimethylenic bromide, and is converted by oxidation into trimethylenic bisulphide, which has previously been obtained by Hagelberg (Abstr., 1890, 949). When the mercaptan is treated with aqueous soda and benzoic chloride, *trimethylenic thiobenzoate*,  $C_3H_6(SBz)_2$ , is formed as a colourless oil. Phthalic anhydride, on the other hand, produces *trimethylenic dithiophthalate*,  $C_6H_4\left(\begin{array}{c} \text{CO} \cdot \text{S} \\ \text{CO} \cdot \text{S} \end{array} \right)C_3H_6$ , which crystallises in lustrous prisms melting at 150—151°. *Trimethylenic dimethylic sulphide*,  $C_3H_6(SMe)_2$ , formed by the methylation of the mercaptan as a colourless oil, is converted by oxidation into *trimethylenedimethylsulphone*,  $C_3H_6(SO_2Me)_2$ , which crystallises in slender needles melting at 155°. *Trimethylenediethylsulphone* is obtained in a similar manner, and crystallises in lustrous plates melting at 184°. *Trimethylenic dibenzyl sulphide* is a colourless oil boiling at 218—221° under 8—9 mm. pressure, and readily yields *trimethylenedibenzylsulphone*, which crystallises in plates

melting at 189°. These disulphones are not hydrolysed by alkalis, and therefore agree with Stuffer's generalisation (Abstr., 1890, 987).  
A. H.

**Cyclic Bisulphides and Disulphones.** By WILHELM AUTENRIETH and K. WOLFF (*Ber.*, 1899, 32, 1375—1390).—Trimethylene mercaptan reacts with formaldehyde to produce *tetramethylene-1:3-bisulphide*,  $C_3H_6\begin{smallmatrix} S \\ \diagup \quad \diagdown \\ S \end{smallmatrix}CH_2$ , as a colourless oil, and by oxidation this is

converted into the corresponding *disulphone*,  $C_3H_6\begin{smallmatrix} SO_2 \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix}CH_2$ , which crystallises in slender needles, melts and decomposes above 300°, and is stable towards acids; the hydrogen atoms of the methylene group situated between the two sulphone groups can be replaced by bromine and alkyl groups. 2:2-Dibromo-1:3-tetramethylenedisulphone crystallises in nacreous plates melting at 288°.

Acetaldehyde yields with the mercaptan 2-methyltetramethylene-1:3-bisulphide,  $C_3H_6\begin{smallmatrix} S \\ \diagup \quad \diagdown \\ S \end{smallmatrix}CHMe$ , as a colourless oil boiling at 79—80° under 8—10 mm. pressure. The corresponding *sulphone*,  $C_3H_6\begin{smallmatrix} SO_2 \\ \diagup \quad \diagdown \\ SO_2 \end{smallmatrix}CHMe$ , crystallises in long needles melting at 261—262°.

*Benzylmethyltetramethylenedisulphone* is obtained by the action of benzylic chloride on the sulphone in presence of alcoholic sodium ethoxide, and crystallises in lustrous plates melting at 158°. Propylaldehyde yields 2-ethyltetramethylenedisulphide as a colourless oil, which is converted by oxidation into the *disulphone*,  $C_3H_6:(SO_2)_2:CHEt$ , melting at 209°. 2-Phenyltetramethylenedisulphide is prepared from benzaldehyde, and crystallises in lustrous plates melting at 70—71°. The corresponding *sulphone* crystallises in slender needles melting at 264—265°, and readily yields a *monobromo-derivative*,  $C_3H_6:(SO_2)_2:CPhBr$ , which crystallises in plates, and melts and decomposes at 233°. These disulphones are hydrolysed by alkalis, one molecule of the latter being required for one of the sulphone, but it has not yet been found possible to isolate the product of the hydrolysis. This behaviour does not conform to Stuffer's generalisation.

Trimethylene mercaptan also forms condensation products with ketones, and these do not yield bromine or alkyl derivatives, both the hydrogen atoms of the methylene group situated between the sulpho-groups having already been replaced. *Dimethyltetramethylene-1:3-bisulphide*,  $C_3H_6:S_2:CMe_2$ , prepared from acetone, is a colourless oil boiling at 79—81° under 8—10 mm. pressure, and is converted by oxidation into the corresponding *disulphone*,  $C_3H_6:(SO_2)_2:CMe_2$ , which crystallises in long prisms melting at 246°. *Methylpropyltetramethylenedisulphide*,  $C_3H_6:S_2:CMePr$ , is obtained from methyl propyl ketone as a colourless liquid, whilst the *disulphone* crystallises in long prisms melting at 202—204°. *Phenylmethyltetramethylenedisulphone* is obtained from acetophenone, and crystallises in slender prisms melting at 260°; it is only attacked with difficulty by fuming nitric acid. *Diphenyltetramethylenedisulphide*,  $C_3H_6:S_2:CPh_2$ , is prepared from benzophenone, and crystallises in lustrous plates melting at 110°;

the *disulphone*, obtained by dissolving the sulphide in benzene and agitating this solution with aqueous permanganate, crystallises in lustrous prisms melting at 256—257°. Ethylic acetoacetate also undergoes condensation with trimethylene mercaptan, yielding the tri-

*methylenemercaptole* of ethylic acetoacetate,  $\text{C}_3\text{H}_6 \begin{smallmatrix} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{CMe} \cdot \text{CH}_2 \cdot \text{COOEt}$ ,

which is a colourless oil and yields a *disulphone* melting at 157°. Ethylenic bromide reacts with sodium trimethylene mercaptide, yielding *pentamethylene-1 : 4-bisulphide*, which is a colourless oil and is converted

by oxidation into *pentamethylene-1 : 4-disulphone*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{SO}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{SO}_2 \cdot \text{CH}_2 \end{smallmatrix}$ , crystallising in slender prisms melting at 282°. This sulphone does not yield bromo- or alkyl derivatives, and, in accordance with Stuffer's rule, is hydrolysed by alkalis. Trimethylenic bromide reacts in a similar manner, yielding *hexamethylene-1 : 5-disulphone*,

$\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{SO}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{SO}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH}_2$ , which crystallises in lustrous prisms melting at 258—259°. This sulphone undergoes hydrolysis when treated with alkalis, and therefore conforms to Stuffer's rule. The corresponding *sulphide* is a colourless oil. A. H.

**Cyclic Compounds, Symmetrical Dimethylethylnaphthene.** By WLADIMIR B. MARKOWNIKOFF and WLADIMIR RUDEWITSCH (*Chem. Centr.*, 1899, i, 176—177; from *J. Russ. Chem. Soc.*, 1898, 30, 586—605).— $\beta$ -Decanaphthene (*J. Russ. Chem. Soc.*, 25, 385) is probably symmetrical dimethylethylnaphthene. By repeatedly fractionating the fraction from petroleum boiling at 155—170°, and treating with fuming sulphuric acid, a portion boiling at 168—170° and containing 2 per cent. of pseudocumene was obtained; from this portion, pure decanaphthene,  $\text{C}_{10}\text{H}_{20}$ , was isolated by means of nitric and sulphuric acids. Decanaphthene boils at 168.5—170° under 752 mm. pressure, has a sp. gr. 0.7929 at 20°/0°, and is not attacked by anhydrous copper sulphate at 300°. By the action of bromine and aluminium bromide at 8°, an oil which does not solidify at -18° and is probably a mixture of the tribromide,  $\text{C}_{10}\text{H}_{11}\text{Br}_3$ , and the tetrabromide,  $\text{C}_{10}\text{H}_{10}\text{Br}_4$ , is obtained. Decanaphthene is not attacked by cold nitric acid of sp. gr. 1.41, but when warmed with the acid for 6 hours it forms an oil which decomposes when distilled under 20 mm. pressure, and when reduced with tin and hydrochloric acid, yields a neutral oil boiling at 210—225° and a mixture of amines boiling at 204—220°. Decanaphthene is dissolved by fuming sulphuric acid at the ordinary temperature, and forms a syrupy sulphonic acid; when boiled with iodine, hydrogen iodide is liberated, and by the action of bromine on the product a substance is obtained which crystallises in needles, melts at 218—220°, and is a mixture of the tribromide,  $\text{C}_{10}\text{H}_{11}\text{Br}_3$ , identical with that obtained from symmetrical dimethylethylbenzene (Jacobson, *Ber.*, 7, 1434) with a small quantity of the dibromide,  $\text{C}_{10}\text{H}_{12}\text{Br}_2$ . The product boiling at 40—182°, formed by the action of iodine on decanaphthene in a sealed tube, contains ethylic iodide, tetrabromometaxylene, and metoctonaphthene; the fraction boiling at 168—182° yields the tribromide,  $\text{C}_{10}\text{H}_{11}\text{Br}_3$ , and by the action of

fuming sulphuric acid a sulphonic acid was obtained from which a hydrocarbon,  $C_{10}H_{14}$ , was prepared. By the action of moist chlorine on decanaphthene, two chlorides,  $C_{10}H_{19}Cl$ , are formed: the one boils at  $213-216^\circ$ , and at  $145-147^\circ$ , under 760 and 110 mm. pressure respectively, and has a sp. gr. 0.9464 at  $20^\circ/0^\circ$ , and 0.9612 at  $0^\circ/0^\circ$ , the other boils at  $216-219^\circ$  and at  $147-149^\circ$  under 760 and 110 mm. pressure respectively, and has a sp. gr. 0.9637 at  $0^\circ/0^\circ$ . A dichloride,  $C_{10}H_{18}Cl_2$ , was also isolated; it boils at  $164-167^\circ$  under 60 mm. pressure and has a sp. gr. 1.0865 at  $20^\circ/0^\circ$  and 1.1022 at  $0^\circ/0^\circ$ . The monochlorides, when heated with sodium acetate at  $250^\circ$ , give 44 per cent of naphthylene with some ethylic acetate, and when heated with quinoline, yield 76 per cent. of naphthylene. The fractions boiling at  $167.5-169^\circ$  and at  $169-171^\circ$  are pure naphthylenes. These compounds combine easily with bromine, forming a dibromide,  $C_{10}H_{18}Br_2$ , which boils at  $135-145^\circ$  under 23 mm. pressure, and some monobromide,  $C_{10}H_{17}Br$ , which boils at  $100-110^\circ$  under 23 mm. pressure. By the action of nitrosyl chloride, the naphthylenes yield oily products. *Acetoxydecanaphthene*, prepared by the action of sodium acetate on the monochloride, has a fruity odour, boils at  $236-239^\circ$ , has a sp. gr. 0.9323 at  $0^\circ/0^\circ$ , and when hydrolysed, yields *decanaphthenol*,  $C_{10}H_{19}\cdot OH$ , which is a colourless liquid, does not solidify at  $-18^\circ$ , boils at  $223.5-225.5^\circ$ , and has a sp. gr. 0.9064 at  $0^\circ/0^\circ$  and 0.8932 at  $20^\circ/0^\circ$ . A *ketone* boiling at  $213-218^\circ$  is obtained by oxidising with potassium dichromate and sulphuric acid, hence decanaphthenol is a secondary alcohol.

The dichloride, when heated with quinoline, yields a terpene,  $C_{10}H_{16}$ , which has the odour of turpentine, is oxidised by exposure to the air, boils at  $173-177^\circ$ , and has a sp. gr. 0.8618 at  $0^\circ/0^\circ$ . A small quantity of an aromatic hydrocarbon,  $C_{10}H_{14}$ , was prepared from the naphthylenes or from decanaphthene chloride by Brühl's reaction.

A *tertiary* and a *secondary nitrodecanaphthene*,  $C_{10}H_{19}NO_2$ , were prepared by Konowaloff's method of nitrating at  $125^\circ$  with nitric acid of sp. gr. 1.075. The former boils at  $146-148^\circ$  under 40 mm. pressure, has a sp. gr. 0.9977 at  $0^\circ/0^\circ$ , 0.9831 at  $20^\circ/0^\circ$ , and a specific refractive index  $n_D$  1.46009 at  $20^\circ$ . The latter boils at  $148-150^\circ$  under 40 mm. pressure, has a sp. gr. at 0.9931 at  $0^\circ/0^\circ$ , 0.9778 at  $20^\circ/0^\circ$ , and a specific refractive index  $n_D$  1.4529 at  $20^\circ$ . *Bromonitrodecanaphthene*,  $C_{10}H_{18}Br\cdot NO_2$ , prepared by the action of bromine on an ice-cold solution of the secondary nitrodecanaphthene in potassium hydroxide solution, has a sp. gr. 1.3740 at  $0^\circ/0^\circ$ , and 1.3552 at  $20^\circ/0^\circ$ .

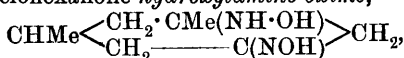
*Tertiary* and *secondary amidodecanaphthenes* are obtained from the corresponding nitro-compounds by reducing with tin and hydrochloric acid. The former is a colourless liquid with an ammonia-like odour, boils at  $199-201^\circ$  under 754 mm. pressure, has a sp. gr. at 0.8675 at  $0^\circ/0^\circ$ , 0.85305 at  $20^\circ/0^\circ$ , and a specific refractive index  $n_D$  1.45209 at  $20^\circ$ . The *hydrochloride* is hygroscopic and crystallises in cubes; the *oxalate* is crystalline and the *platinochloride*, *aurichloride*, and *formate* are syrups. Secondary amidodecanaphthene boils at  $202-204^\circ$  under 754 mm. pressure, has a sp. gr. 0.8683 at  $0^\circ/0^\circ$ , 0.85499 at  $20^\circ/0^\circ$ , and a specific refractive index  $n_D$  1.45679 at  $20^\circ$ ; the *platinochloride* and the *oxalate* were prepared.



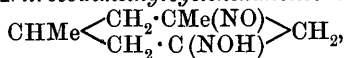
Ketones were isolated from the neutral reduction products obtained by distilling in steam. The *ketone* from tertiary amidodecanaphthene boils at 200—210°, whilst the *ketone* from secondary amidodecanaphthene boils at 200—215°. Some naphthylene and alcohols were also formed.

By the action of potassium nitrite on tertiary amidodecanaphthene, the naphthylene which boils at 167·5—171°, and has a sp. gr. 0·8316 at 0°/0°, and *tertiary naphthenol* were obtained. The latter boils at 204—206° under 749 mm. pressure, and by the action of phosphorus pentachloride yields the naphthylene which boils at 168—171°, and a tertiary chloride which decomposes on distillation. A mixture of secondary and tertiary naphthenols boiling at 207—210° is obtained from secondary amidodecanaphthene. According to Markownikoff, since the tertiary naphthene chlorides decompose on boiling, the monochlorides which boil at 213—219° are secondary chlorides derived probably from  $C_6H_8Me_2Et$  [ $Et : Me_2 = 1 : 3 : 3$ ]. E. W. W.

**Hydroxylamino-oximes of certain Cyclohexenones.** By CARL D. HARRIES and ISRAEL MATFUS (*Ber.*, 1899, 32, 1340—1342).—3 : 5-Dimethylcyclohexanone *hydroxylamino-oxime*,

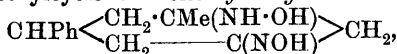


prepared by the action of hydroxylamine (2 mols.) dissolved in methylic alcohol on dimethylcyclohexenone, crystallises in needles and melts at 155—158°; it may be crystallised from water, and dissolves readily in acids and alkalis, developing an intense blue coloration with oxidising agents. *Nitrosodimethylcyclohexanoneoxime*,



which is thus produced, decomposes at 125°, and becomes blue at about 100°; dilute sulphuric acid liberates gas, and converts it into the oxime of dimethylcyclohexenone (Knoevenagel, *Abstr.*, 1895, i, 52).

5 : 3-Phenylmethylcyclohexanone *hydroxylamino-oxime*,



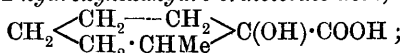
crystallises in colourless prisms melting at 151—152° when slowly heated, and at 165° when the temperature rises more rapidly; oxidising agents develop an intense blue coloration.

3 : 5-Methylisopropylcyclohexanone (metacamphor) *hydroxylamino-oxime*,  $CHPr \begin{array}{c} \text{CH}_2 \cdot CMe(NH \cdot OH) \\ \text{CH}_2 \text{---} C(NO\cdot H) \end{array} > CH_2$ , crystallises from benzene in prismatic needles and melts at 105°; it dissolves readily in dilute acids and in alkalis, yielding an oily oxime when treated with hot dilute sulphuric acid.

Camphenone fails to produce a hydroxylamino-oxime when treated with hydroxylamine. M. O. F.

**Bromohexahydro-orthotoluic Acid and its Derivatives.** By W. SERNOFF (*Ber.*, 1899, 32, 1167—1175).—Unlike the meta-acid (this vol., i, 422), hexahydro-orthotoluic acid, when acted on with

bromine in presence of phosphorus, yields only one *bromo-acid*,  
 $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CBr} \cdot \text{COOH}$ ; this melts at  $97^\circ$ , crystallises in monoclinic crystals [ $a:b:c = 1.2560:1:1.4593$ ;  $\beta = 113^\circ 8'$ ; sp. gr. 1.574 at  $19^\circ$ ], dissolves easily in acetone, ether, or alcohol, less readily in benzene, and is insoluble in water. Its salts cannot be prepared, since the action of alkalis leads immediately to the formation of salts of 2-hydroxyhexahydro-orthotoluic acid,



this crystallises from benzene and melts at  $109^\circ$ , it dissolves readily in acetone, less readily in cold petroleum, benzene, and water, and forms a series of well-defined salts. By the action of alcoholic soda on the bromo-acid, 2-ethoxyhexahydro-orthotoluic acid is produced, together with a certain amount of an unsaturated acid; it crystallises from formic acid or aqueous acetone, and melts at  $81^\circ$ .

$\Delta^2$ -Tetrahydro-orthotoluic acid,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CH} \\ \text{CH}_2 \cdot \text{CHMe} \end{smallmatrix} \text{C} \cdot \text{COOH}$ , is produced, together with the hydroxy-acid already referred to, by the action of boiling alkali on the bromo-acid, and is readily separated by extracting the aqueous solution with light petroleum, from which it crystallises in long needles melting at  $87^\circ$ ; it decolorises potassium permanganate solution, combines with hydrogen bromide, and forms a *dibromide* which crystallises from benzene and melts at  $155\text{--}156^\circ$ ; the same acid is also produced by heating the bromo acid with quinoline at  $150^\circ$ , or with formic acid at  $100^\circ$ . By reduction with zinc-dust and hydrochloric acid, the bromo-acid gives an oily product which is regarded as *cis-hexahydro-orthotoluic acid*; the *anilide* from this melted at  $109\text{--}111^\circ$ , whilst that from the isomeric crystalline acid melted at  $153^\circ$ .  
 T. M. L.

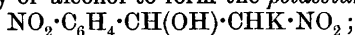
**Action of Bromine on Monochlorobenzene in Presence of Anhydrous Aluminium Chloride.** Preparation of Parabromochlorobenzene. By A. MOUNEYRAT and CH. POURRET (*Bull. Soc. Chim.*, 1898, [iii], 19, 801—803).—If anhydrous aluminium chloride is gradually added to a mixture of chlorobenzene and bromine at  $0^\circ$ , there is an abundant evolution of hydrogen bromide, and parachlorobromobenzene is formed to the extent of at least 95 per cent. of the theoretical yield.  
 N. L.

**Condensation of Nitromethane with Aromatic Aldehydes.** By JOHANNES THIELE (*Ber.*, 1899, 32, 1293—1295).—Alcoholic potash brings about the condensation of nitromethane with aromatic aldehydes in the same way that potassium carbonate causes its condensation with aldehydes of the fatty series; in the first instance, the potassium salt of the condensation product is formed, which, when acidified, passes into the styrene derivative.

*o*-Nitrostyrene, prepared from benzaldehyde and nitromethane, crystallises from alcohol in yellow prisms melting at  $58^\circ$ .

*o*-Metadinitrostyrene, prepared from metanitrobenzaldehyde, separates from alcohol in yellow needles which melt at  $125^\circ$ .

In the same way, orthonitrobenzaldehyde condenses in the presence of a small quantity of alcohol to form the *potassium salt*,



this crystallises in orange leaflets which lose water and turn yellow in a desiccator. *Orthonitrophenylnitroethanol* is precipitated as a yellow oil on acidifying the aqueous solution; on treatment with ferrous sulphate and sodium hydroxide, this substance is converted into a blue dye (indigo?); the *acetyl* derivative separates from alcohol in white needles melting at  $109^\circ$ .

*ω-Paradinitrostyrene*, prepared from paranitrobenzaldehyde, separates from alcohol in yellow needles melting at  $196-199^\circ$ .

*Paraphenylene-bis-nitroethylene*,  $\text{C}_6\text{H}_4(\text{CH}:\text{CH} \cdot \text{NO}_2)_2$ , prepared from terephthalaldehyde and nitromethane, separates as a yellow, flocculent precipitate when its white potassium salt is acidified, and crystallises from hot alcohol in glistening, orange crystals, which melt and decompose between  $200-230^\circ$ .

*Paraphenylene-bis-nitroethanol*,  $\text{C}_6\text{H}_4[\text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NO}_2]_2$ , separates from an alcoholic solution as a light yellow, crystalline powder, which melts and decomposes at  $163-168^\circ$ . J. F. T.

**Action of Carbonic Anhydride on the Sodium Derivatives of the Nitrophenols.** By PAUL MONNET and LOUIS BENDA (*Bull. Soc. Chim.*, 1898, 19, [iii], 688—692).—The action between sodium carbonate and the nitrophenols is a reversible one, for the sodium derivative of ortho- or meta-nitrophenol, when dissolved in cold water, is decomposed by excess of carbonic anhydride, and the free nitrophenol is precipitated almost quantitatively. The meta-compound is the more soluble, and on allowing some of the carbonic anhydride to escape from the filtrate, the colour of the latter darkens perceptibly, indicating a reversion to the sodium derivative; when more of the gas is bubbled through the solution, this action is again reversed and a further precipitate of metanitrophenol is obtained.

When a cold solution of the neutral sodium derivative of paranitrophenol is saturated with carbonic anhydride, the relatively insoluble acid derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{ONa}$ ,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , is precipitated; if, however, the solution is sufficiently dilute, this compound remains dissolved, and the action goes on until the free nitrophenol is obtained.

G. T. M.

**Dihydroanethoil.** By AUGUST KLAGES (*Ber.*, 1899, 32, 1436—1441).—Anethoil,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{CH} \cdot \text{CH}_3$ , can be reduced with sodium and alcohol to paraprophenylic methylic ether,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$ . From this, the phenol itself was prepared by treatment with hydriodic acid and phosphorus at  $180^\circ$ ; its *tribromo*-derivative melts at  $56^\circ$ . The *sulphonic acid*,  $\text{C}_{10}\text{H}_{13}\text{O} \cdot \text{SO}_3\text{H}$ , was prepared by treatment of the ether with strong sulphuric acid; it crystallises with  $1\text{H}_2\text{O}$ , and melts at  $94-96^\circ$ ; when crystallised from strong sulphuric acid, it is obtained anhydrous, and then melts at  $120-122^\circ$ ; the anhydrous salt absorbs water from the air and regenerates the monohydrate. The *barium salt* of the acid, the oily *sulphonic chloride*, and the *sulphonamide* melting at  $133^\circ$  were also prepared. Paraprophenylic methylic ether, prepared as above, is not identical with Landolph's

dihydroanethoil (Abstr., 1880, 384), which must therefore have some other constitution.

Asarone,  $C_6H_2(OMe)_3 \cdot CH:CH \cdot CH_3$  (Gattermann, this vol., i, 347), is reduced by sodium and alcohol to propyltrihydroxyphenylic trimethylic ether,  $C_6H_2(OMe)_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 [C_3H_7 : (OMe)_3 = 1 : 2 : 4 : 5]$ ; this boils at  $159-160^\circ$  and  $258-260^\circ$  under pressures of 38 mm. and 1 atmo. respectively, melts below  $0^\circ$ , and has a sp. gr.  $1.038$  at  $16^\circ/4^\circ$  (Ciamician and Silber have already prepared an impure dihydroasarone boiling at  $260-274^\circ$ ). Esdragole,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CH:CH_2$ , which contains a  $\cdot CH_2 \cdot CH:CH_2$  and not a  $\cdot CH:CH \cdot CH_3$ -group, cannot be reduced with sodium and alcohol. C. F. B.

**Mixed Guaiacylic Alkylic Carbonates.** By ALBERT MOREL (*Bull. Soc. Chim.*, 1898, [iii], 19, 890-893. Compare this vol., i, 29).—Mixed phenylic alkylic carbonates are readily obtained by the action of alcohols of the fatty series on phenylic carbonate in presence of organic bases, but this method of preparation is of much less value in the case of the mixed guaiacylic alkylic carbonates on account of the great stability of guaiacylic, as compared with phenylic, carbonate. The reaction appears, however, to be more readily brought about with alcohols of high molecular weight. The following compounds were prepared by the action of sodium alkyloxides on guaiacylic carbonate dissolved in a mixture of ether with the desired alcohol:

*Guaiacylic methylic carbonate* is a colourless liquid of aromatic odour, boiling at  $240^\circ$  under the ordinary pressure and at  $165^\circ$  under 60 mm.; it has a sp. gr.  $1.196$  at  $0^\circ$ .

*Guaiacylic ethylic carbonate*, a colourless liquid having an agreeable odour of vanilla, boils at  $145^\circ$  under 30 mm., and at  $175-180^\circ$  under 50 mm. pressure; it has a sp. gr.  $1.150$  at  $0^\circ$  and  $1.123$  at  $20^\circ$ .

*Guaiacylic propylic carbonate* is a colourless liquid boiling at  $201-202^\circ$  under 90 mm. pressure, and has a sp. gr.  $1.116$  at  $0^\circ$ .

*Guaiacylic isobutylic carbonate* is a colourless liquid boiling at  $195-210^\circ$  under 50-60 mm. pressure, and has a sp. gr.  $1.092$  at  $0^\circ$ .

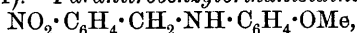
*Guaiacylic isoamyllic carbonate* boils at  $200-210^\circ$  under 60 mm. pressure, and has a sp. gr.  $1.081$  at  $0^\circ$ . N. L.

**Occurrence of Cholesterol in the Products of the Beet Sugar Manufacture.** By EDMUND O. VON LIPPMANN (*Ber.*, 1899, 32, 1210-1212. Compare Abstr., 1888, 315).—Cholesterol has been isolated from the froth formed on a waste liquor from the treatment of crude beet sugar. This substance is identical with ordinary cholesterol, and differs entirely from the phytosterol previously isolated by the author. A. H.

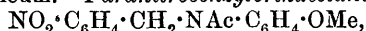
**Heterocyclic Nuclei containing Iodine in Organic Compounds.** By CONRAD WILLGERODT (*J. pr. Chem.*, 1899, [ii], 59, 198-203. Compare Abstr., 1893, i, 256, 505, 561; 1895, i, 230).—The only heterocyclic nuclei containing iodine yet known are the so-called aromatic orthiodoso-carboxylic or -sulphonic acids; attempts have been made to obtain a ring containing carbon, nitrogen and iodine, but, so far, without success. By the action of chlorine on paranitroorthiod-aniline, beautiful, golden-yellow lamellæ of *paranitroorthochlororthiod-*

*aniline* were obtained, melting at  $195^{\circ}$ , instead of the desired heterocyclic compound.  
F. H. N.

**Retardation of Chemical Reactions. I. Paranitrobenzylic Bases.** By CARL PAAL and C. BENKER (*Ber.*, 1899, 32, 1251—1258. Compare Kromschröder and Paal, *Abstr.*, 1897, i, 115; Paal and Sprenger, *ibid.*, 184).—*Paranitrobenzylorthanisidine*,



is readily obtained when a concentrated alcoholic solution of paranitrobenzylic chloride (1 mol.) and orthanisidine (2 mols.) is boiled for some 4 hours; it forms red, compact crystals melting at  $95^{\circ}$ , and readily soluble in most warm organic solvents. When boiled with five times its weight of anhydrous formic acid, it is converted into *paranitrobenzylorthoformanisidine*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{CHO}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , which crystallises from alcohol in long, yellowish plates melting at  $102^{\circ}$ , and is readily soluble in most organic solvents, with the exception of light petroleum. *Paranitrobenzylorthacetanisidine*,

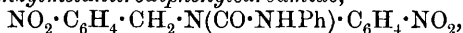


crystallises in yellow plates melting at  $78^{\circ}$ .

*Paranitrobenzylorthonitraniline*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , is obtained when its generators are boiled in concentrated alcoholic solution for 10 hours or are heated with anhydrous sodium carbonate for 1—2 hours at  $130$ — $140^{\circ}$ ; it forms reddish-brown needles melting at  $145^{\circ}$  and destitute of basic properties.

*Paranitrobenzylmetanitraniline* is formed together with *bisparanitrobenzylmetanitraniline* when the components are heated in an oil-bath at  $130$ — $140^{\circ}$ , and may be separated by means of hot alcohol in which the bis-compound is practically insoluble; the former crystallises in pointed, reddish-brown prisms melting at  $151^{\circ}$ ; *paranitrobenzylmetaformonitraniline* crystallises in brownish, compact needles melting at  $104^{\circ}$ , and its *acetyl* derivative in colourless, glistening, flat needles melting at  $178^{\circ}$ . *Bisparanitrobenzylmetanitraniline*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , crystallises in brown-red needles melting at  $235^{\circ}$ . *Paranitrobenzylparanitraniline*, obtained by heating the components in a sealed tube at  $140$ — $145^{\circ}$ , crystallises in yellow needles melting at  $192^{\circ}$ ; its *formyl* derivative crystallises in pale yellow, concentrically arranged, flat needles melting at  $135^{\circ}$ , and its *acetyl* derivative in flat needles melting at  $145^{\circ}$ . Phenyl isocyanate combines slowly with paranitrobenzylorthanisidine, the combination being best effected by heating with a small quantity of benzene in sealed tubes at  $100^{\circ}$ . *Paranitrobenzylorthanisylphenylcarbamide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{CO} \cdot \text{NHPh}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , so obtained, crystallises in yellow, satiny plates melting at  $110^{\circ}$ .

*Paranitrobenzylmetanitrodiphenylcarbamide*,



forms yellow plates melting at  $126^{\circ}$ .

Several instances of the protective influence of ortho-substituents were observed:—For example, the yield of paranitrobenzylorthonitraniline is better than that of orthonitrobenzylorthonitraniline; again, the orthonitro-group in paranitrobenzylorthonitraniline completely hinders the formation of a formyl or of an acetyl derivative, and also prevents the compound from combining with phenyl isocyanate.

cyanate to form a substituted carbamide. Contrary to expectation, it has not been found possible to combine the isocyanate with paranitrobenzylparanitraniline. J. J. S.

**Preparation of Pure Tertiary Anilines and Tetralkylated Aromatic Diamines.** By JOHANNES PINNOW (*Ber.*, 1899, 32, 1401—1408. Compare Abstr., 1898, 133, 184).—The hydrochloride, or occasionally the hydrobromide, of the primary amine,  $R' \cdot NH_2$  or  $R''(NH_2)_2$ , is heated with methylic alcohol in a sealed tube for several hours at temperatures between  $145^\circ$  and  $195^\circ$ . In some cases, namely, those in which the ortho-position relatively to the amido-group is occupied, no addition of methylic chloride and consequent formation of a quaternary ammonium salt occurs. In the case of benzidine, tetramethylbenzidine hydrochloride methochloride was formed. In all cases, the product of the reaction could be made to yield the tertiary amine,  $R' \cdot NMe_2$ , or tetralkylated diamine,  $R''(NMe_2)_2$ , by heating it with ammonia for 2—3 hours at  $110$ — $140^\circ$  in the case of monamines and amidocarboxylic acids, or for an hour at  $180$ — $190^\circ$  in the case of diamines and amidophenols.

The following primary amines were experimented with:—Ortho-, meta-, and para-phenylenediamines, benzidine,  $\alpha$ - and  $\beta$ -naphthylamines, orthamidophenol, and paramidobenzoic acid. The last acid can be prepared by heating dimethylparatoluidine with hydrochloric acid and methylic alcohol, oxidising the methochloride with permanganate, and then removing methylic chloride by heating with ammonia.

C. F. B.

**Relation of Tervalent to Quinquevalent Nitrogen.** By ARTHUR LACHMAN (*Amer. Chem. J.*, 1899, 21, 433—446. Compare Abstr., 1898, i, 400).—The author has examined the behaviour of zinc ethyl towards a series of compounds in the hope of throwing light on the question of the constitution of the nitro-group.

Diethylnitrosamine and phenylmethylnitrosamine do not react with zinc ethyl. Diphenylnitrosamine is violently attacked, and yields a well-characterised additive compound, probably having the constitution  $NPh_2 \cdot NEt_2 \cdot \begin{smallmatrix} Zn \\ \diagup \quad \diagdown \\ O \end{smallmatrix}$ , which is decomposed by water, yielding zinc hydroxide, diphenylamine, and a volatile base, doubtless diethylhydroxylamine.

Zinc ethyl acts violently on nitrosobenzene, yielding as the chief products azoxybenzene and phenylhydroxylamine, together with small quantities of aniline and ethylaniline, and a considerable quantity of a black, neutral tar. Azoxybenzene does not react with zinc ethyl even after fourteen days, and as this appears to exclude Brühl's formula, it is concluded that azoxybenzene has the structure usually assigned it,

namely,  $O \cdot \begin{smallmatrix} NPh \\ | \\ NPh \end{smallmatrix}$ .

Dimethylnitramine is not attacked by zinc ethyl, hence it is probable that its structure is  $NMe_2 \cdot N \cdot \begin{smallmatrix} O \\ | \\ O \end{smallmatrix}$ . Nitroethane yields trimethylamine oxide, as stated by Bewad (Abstr., 1889, 112), whilst nitrobenzene is only partly altered. This points to the conclusion that the nitro-

group in nitroethane and nitrobenzene is differently constituted, the former being probably  $\text{O}:\text{N}(\text{Et})\text{O}$ , and the latter probably  $\text{Ph}:\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ .

A. I.

**Orth-azoxy- Azo- and Hydrazo-anisoil, and Dianisidine.** By PAUL STARKE (*J. pr. Chem.*, 1899, [ii], 59, 204—227).—By reducing orthonitranisoil with sodium methoxide, *orthoazoxyanisoil* was obtained; it melts at  $81^\circ$  and crystallises in orange-yellow prisms soluble in alcohol, ether, benzene, &c. Using sodium amalgam as the reducing agent in methylic alcohol solution at a temperature below  $50^\circ$ , orange-red prisms of *orthoazoanisoil* were formed, melting at  $141^\circ$ , and easily soluble in concentrated hydrochloric acid, hot alcohol, ether, acetone, &c.; this, when reduced by ammonium sulphide, yields *orthohydrazoanisoil*, which crystallises in colourless plates, becomes red on exposure to air, and melts at  $102^\circ$ .

Hydrochloric acid brings about intramolecular transformation of hydrazoanisoil into dianisidine, which forms colourless plates melting at  $131.5^\circ$ ; the latter compound was also obtained by reducing orthonitranisoil with zinc dust in alkaline solution. The nitrate, platinum-chloride, sulphate, and chromate are described. The *diacetyl* derivative forms colourless prisms and melts at  $231^\circ$ ; the *dibenzoyl* derivative melts at  $236^\circ$ ; the *carbamide*,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{OMe} \\ \text{NH} \cdot \text{C}_6\text{H}_3 \cdot \text{OMe} \end{smallmatrix}$ , and *thiocarbamide*, are both amorphous and decompose when heated. *Dinitrodiaceto-dianisidide*, formed by nitrating the diacetyl derivative, crystallises in yellow tablets and decomposes at  $220^\circ$ . On nitrating dianisidine, the nitro-group enters each ring in the meta-position relatively to the amido-group; the *dinitro*-compound so obtained crystallises in needles. On diazotisation, dianisidine yields very stable diazo-derivatives; *tetrazodianisyl sulphate* explodes at  $149^\circ$ ; the *chloride*, when heated, gradually chars. When the chloride is treated with sodium sulphite in aqueous solution, it yields *sodium tetrazodianisylsulphonate*, which crystallises, with  $3\text{H}_2\text{O}$ , in yellow needles, and when reduced with zinc dust and acetic acid, is converted into the *dianisyl dihydrazinesulphonate*; this forms colourless, prismatic crystals. *Dianisyl*,  $\text{C}_{12}\text{H}_8(\text{OMe})_2$ , was best obtained by heating the tetrazo-sulphate with absolute alcohol; it forms large, almost colourless prisms which melt at  $35.5^\circ$ .

F. H. N.

**Action of Diazo-compounds on Oximes.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1546—1548).—The compounds formed by the condensation of 2 mols. of an oxime with one of a diazo-compound which were first prepared by Mai (Abstr., 1892, 163, 1079) are very similar in their properties to those azohydroxyamides prepared by the author from  $\beta$ -substituted derivatives of hydroxylamine and diazonium salts, the most characteristic reaction of these compounds, namely, their behaviour towards ferric chloride, being identical in each case. He therefore considers that the most probable constitution for Mai's compounds is  $\text{CMe}_2:\text{N} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{N}(\text{OH}) \cdot \text{N}_2\text{Ph}$ , diazobenzene and the oxime first uniting to form a compound,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{N}(\text{OH}) \cdot \text{N}_2\text{Ph}$ , which

then reacts with a second molecule of the oxime to form Mai's compound, the elements of water being eliminated.

The close resemblance between these substances is still more pronounced in cases where the diazonium salt contains a nitro-group in the para-position, thus the compound,  $\text{CMe}_2 \cdot \text{N} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{N}(\text{OH}) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ,

behaves very similarly to the azohydroxyamide,  $\text{OH} \cdot \text{NR} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ; the former, which is precipitated on the addition of acetoxime to a solution of paranitrodiazobenzene acetate, crystallises in light yellow, glistening leaflets, melts, when not too quickly heated, at  $153-154^\circ$ , and dissolves in alkalis with a deep red coloration. With ferric chloride in alcoholic solution, it gives a bluish-green coloration which slowly disappears, and with copper acetate, a brownish-yellow, crystalline copper salt sparingly soluble in alcohol. J. F. T.

**Preparation of Acyl- and Nitroso-derivatives of Aromatic Alkylcarbamides.** By REINHOLD WALTHER and ST. WLODKOWSKI (*J. pr. Chem.*, 1899, [ii], 59, 266—286).—Pyridine may be used with great advantage to assist in the introduction of acyl groups into substituted carbamides and similar compounds (compare Deninger, Abstr., 1895, i, 461; Einhorn and Hollandt, Abstr., 1898, i, 577).

When a mixture of carbamide and pyridine is heated on the water-bath and benzoic chloride is added gradually, the temperature of the whole rises and the carbamide passes into solution. The product may be isolated by pouring the mixture into water, when it separates in a crystalline form, and may be purified by crystallisation from acetic acid; it melts at  $215-216^\circ$ , and its composition and properties indicate that it is a benzoylbiuret; it does not, however, give a violet-red coloration with alkaline copper sulphate (compare Schiff, Abstr., 1898, i, 243).

Benzoic chloride acts on guanidine in presence of excess of soda, yielding *dibenzoylcarbamide*,  $\text{CO} \cdot (\text{NH} \cdot \text{CO} \cdot \text{Ph})_2$ , which crystallises from boiling absolute alcohol in small, white needles and melts at  $210^\circ$ .

Benzophenylcarbamide,  $\text{NPhBz} \cdot \text{CO} \cdot \text{NH}_2$ , is made by dissolving phenylcarbamide in pyridine and adding benzoic chloride drop by drop; on pouring the mixture into water, the product is deposited as a flocculent precipitate; it crystallises from hot absolute alcohol in slender, white, felted needles and melts at  $203-204^\circ$ .

*Acetophenylcarbamide* is made in a similar manner, but the temperature must be kept low; it crystallises from boiling absolute alcohol in slender, white needles and melts at  $183-184^\circ$ .

Orthotolylcarbamide, prepared by the action of potassium cyanate on orthotoluidine acetate, crystallises from boiling absolute alcohol in shining, white leaflets and melts at  $190-191^\circ$  (Cosack, Abstr., 1880, 713, gives  $185^\circ$ ). Benzorthotolylcarbamide crystallises in slender, small needles and melts at  $210^\circ$  (compare Gattermann and Cantzler, Abstr., 1892, 832). *Acetorthotolylcarbamide* melts at  $168-169^\circ$ .

Metatolylcarbamide forms white, shining needles melting at  $142-143^\circ$  (compare Cosack, Abstr., 1880, 245, 713).

*Paratolylcarbamide* separates from boiling water in white needles and melts at  $181-182^\circ$ . *Acetoparatolylcarbamide* melts at  $199-200^\circ$ .

Metaxylylcarbamide, made by treating metaxylylidine acetate with



potassium cyanate, crystallises from boiling absolute alcohol in white, silky tablets and melts at 206—207° (Genz, *Ber.*, 1870, 3, 226, gives 186°). *Benzometaxylylcarbamide* crystallises in long, thin, felted needles melting at 220—221°, and *acetometaxylylcarbamide* in small, white needles melting at 201—202°.

$\beta$ -Naphthylcarbamide crystallises in slender, white needles, melts at 213—214°, resolidifies at 215—220°, and melts once more at 300°, but decomposes simultaneously (compare Cosiner, *Abstr.*, 1881, 605). Attempts to prepare its acetyl and benzoyl derivatives were unsuccessful, as was also the case with  $\alpha$ -naphthylcarbamide. The latter substance melts at 213—214°, solidifies at 215—220°, and finally melts and decomposes at 295—296°.

When  $\alpha$ - or  $\beta$ -naphthylcarbamide is heated at 220°, decomposition occurs, the corresponding dinaphthylcarbamide and carbamide being formed.  $\beta$ -Dinaphthylcarbamide is amorphous, is not dissolved by any solvent, and melts and decomposes above 300°.  $\alpha$ -Dinaphthylcarbamide melts at 295—296° (compare Pagliani, *Abstr.*, 1879, 723; Hahn, *Abstr.*, 1886, 1035).

Metanitrophenylcarbamide forms beautiful, yellow needles and melts indefinitely at 187—194° (compare Hofmann, *Annalen*, 1848, 67, 156, and 1849, 70, 137). The corresponding ortho- and para-nitro-derivatives could not be prepared.

*Nitrosophenylcarbamide*,  $\text{NO} \cdot \text{NPh} \cdot \text{CO} \cdot \text{NH}_2$ , is made by the action of sodium nitrite on a solution of phenylcarbamide in glacial acetic acid, and can be purified by dissolution in ether and precipitation with light petroleum. It forms light yellow needles, melts and decomposes at 95°, is very readily soluble in alcohol, less readily in alcohol and benzene, insoluble in petroleum, and cannot be kept, as it readily undergoes decomposition, even in a vacuum; when warmed with water, it dissolves and decomposes with evolution of gas, and the odour of phenol becomes evident.

*Nitrosometatolylcarbamide* crystallises in light yellow needles and melts and decomposes at 80°; like the preceding compound, it is very unstable.

*Nitrosoparatolylcarbamide* crystallises in yellow needles and melts and decomposes at 83°.

*Nitroso- $\beta$ -naphthylcarbamide*,  $\text{C}_{10}\text{H}_7 \cdot \text{N}(\text{NO}) \cdot \text{CO} \cdot \text{NH}_2$ , melts and decomposes at 122—123°. Metanitrophenylcarbamide does not yield a nitroso-derivative.

Nitrosophenylcarbamide does not yield a hydrazine on reduction with zinc dust and acetic acid, but is decomposed into nitrous acid and phenylcarbamide.

A. L.

**Action of Fuming Nitric Acid on some Synthetically Prepared Cyclic Compounds.** By HERMANN KUNZ-KRAUSE (*Chem. Centr.*, 1899, i, 119—120; from *Pharm. Zeit.*, 1898, 43, 838—840).—In continuation of work on Vitali's reaction (*Pharm. Zeit.*, 43, 828—831), the author has determined the behaviour of anilides with fuming nitric acid at 100°. The product obtained from acetanilide ignites spontaneously, and this property is also exhibited by the products from derivatives which contain strongly electro-negative groups

or a methyl group in the ortho-position. The following derivatives, however, do not yield spontaneously inflammable products:—derivatives containing (1) electro-positive groups (Me, OMe, OEt, or OH), salt residues ( $\text{SO}_3\text{Na}$ ), or complicated acid residues [ $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CO}$ ] in the para-position; (2) an OH-group in the ortho-position; (3) the hydrogen atom of the acetamide group replaced by a methyl group; (4) the acetyl group replaced by another acid group, or (5) the benzene replaced by a naphthalene or quinoline ring.

Parabromacetanilide may be prepared by adding a concentrated aqueous solution of bromine to a cold solution of acetanilide in water until the solution becomes yellow and crystallising the precipitate from hot water.

E. W. W.

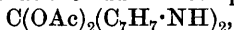
**Isocarbamide Ethers [Imidocarbamates] and other Derivatives of Carbamide.** By FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1899, 21, 136—192. Compare Lengfield and Stieglitz, *Abstr.*, 1894, i, 333).—Carbodiorthotolylimide,  $\text{C}(\text{N}\cdot\text{C}_7\text{H}_7)_2$ , first prepared by Will and Bielschowski (*Abstr.*, 1882, 1091), is an oil which boils at  $200^\circ$  under 15 mm. pressure, and has an index of refraction 1.624. It rapidly polymerises to a white solid. When heated with methylic alcohol at  $180^\circ$  to  $190^\circ$ , it gives *methylicisodiorthotolylcarbamide* (*methylic orthotolylimido-orthotolylcarbamide*),  $\text{C}_7\text{H}_7\cdot\text{N}\cdot\text{C}(\text{NH}\cdot\text{C}_7\text{H}_7)\cdot\text{OMe}$ , which is obtained as an oil boiling at  $206^\circ$  under 18 mm. pressure, refractive index 1.592; after some months, one specimen of the oil deposited long needle-shaped crystals of the ether, which melted at  $48.5^\circ$ . The *hydrochloride*, probably  $\text{OMe}\cdot\text{CCl}(\text{NH}\cdot\text{C}_7\text{H}_7)_2$ , is a white, crystalline solid insoluble in ether, benzene, or light petroleum; it decomposes slowly in moist air, and rapidly on heating with water, leaving a residue of diorthotolylcarbamide; a similar decomposition is produced by heating in a current of carbonic anhydride, or in a current of dry hydrogen chloride at  $90^\circ$ , when methylic chloride is eliminated quantitatively. The *platinochloride* forms hard, red crystals, and melts at  $155^\circ$  with decomposition. *Ethylic orthotolylimido-orthotolylcarbamide* is a colourless oil which boils at  $215.5^\circ$  under 24 mm. pressure, but does not solidify at  $-5^\circ$ , and has a refractive index 1.606. The *propylic* salt is a colourless oil boiling at  $212$ — $214^\circ$  under 14 mm. pressure; the *isobutylic* salt is a colourless oil boiling at  $218^\circ$  under 18 mm. pressure; the *isoamylic* salt is a colourless oil boiling at  $206^\circ$  under 10 mm. pressure, and has an index of refraction 1.572.

*Carbodioparatolylimide* is a pale yellow oil boiling at  $221$ — $223^\circ$  under 20 mm. pressure. *Methylic paratolylimidoparatolylcarbamide* is an oil boiling at  $220^\circ$  under 15 mm. pressure; the *propylic* salt boils at  $221^\circ$  under 16 mm. pressure; the *isoamylic* salt boils at  $210^\circ$  under 15 mm. pressure, and has an index of refraction 1.594.

Carbodiphenylimide forms a yellow *monoplatinochloride* which begins to decompose at  $143^\circ$ , and melts to a reddish oil at  $150^\circ$ ; the *diplatinochloride* forms reddish-brown needles which do not melt at  $250^\circ$ . *Carbodiorthotolylimide dichloride* is a white solid, insoluble in light petroleum or benzene, but soluble in chloroform; it melts with decomposition at  $235$ — $237^\circ$ , and is decomposed by moisture into hydrogen chloride and diorthotolylcarbamide. The *monoplatino-*

*chloride* is yellow, decomposes at 146—148°, and melts at 155°. *Carbodiparatolylimide monoplatinochloride* is a yellow salt which begins to decompose at 148°, and melts completely between 155° and 160°. *Carbodiparatolylimide sesquichloride* is a crystalline salt melting at 126—127°. *Carboallylphenylimide sesquichloride* is also a crystalline salt.

By the action of acetic or formic acids on carbodiorthotolylimide, ditolylcarbamide is produced, together with acetic anhydride or carbonic oxide. It is suggested that the additive compound,



is formed as an intermediate product.

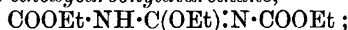
Phenylallylcarbamide,  $\text{C}_3\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , melts at 113°, and not at 97° as stated by Maly (*Zeit. Chem.*, 1869, [ii], 5, 258); it is also shown that the substance melting at 105° which was prepared by Bizio (*J. prakt. Chem.*, 1862, 86, 292) by desulphurising phenylallylthiocarbamide is phenylallylcarbamide, and not carboallylphenylimide, as has usually been assumed. *Carboallylphenylimide*,  $\text{C}_3\text{H}_5\cdot\text{N}:\text{C}:\text{NPh}$ , was obtained as an oil which could not be purified owing to its instability; it gave, however, an unstable imidocarbamate by the action of alcohol and sodium ethoxide, formed a definite sesquichloride, and was decomposed in the normal way by formic acid, giving phenylallylcarbamide and carbonic oxide.

Unlike the imido-ethers, the imidocarbamates are very stable towards water; by the action of cold dilute hydrochloric acid, methylic orthotolylimidotolylcarbamate gives ditolylcarbamide, and a small amount of tritolylguanidine; ethylic phenylimidophenylcarbamate behaves in a similar manner. By the action of acetic acid, methylic orthotolylimidotolylcarbamate gives ditolylcarbamide and methylic acetate. Concentrated sulphuric acid acting on ethylic phenylimidophenylcarbamate gives aniline, alcohol, and carbonic anhydride, but no trace of phenylurethane. Unlike the imido-ethers, the imidocarbamates are only acted on with difficulty by ammonia, but on heating together at 200° the corresponding guanidine is produced. On heating ethylic phenylimidophenylcarbamate at 295—300°, ethylene sulphide is given off, and the residue contains carbanilide and polymerised carbodiphenylimide; it is therefore probable that the combination of alcohol with carbodiphenylimide is reversed at high temperatures. The imidocarbamates are not decomposed by boiling with potassium hydroxide, but at 160° methylic orthotolylimidotolylcarbamate is converted into toluidine, methylic alcohol, and carbonic anhydride. Ethylic phenylimidophenylcarbamate, when heated in a current of hydrogen sulphide at 190°, is converted into aniline, carbon bisulphide, and ethylic alcohol, together with a certain amount of diphenylcarbamide and mercaptan, and when heated with carbon disulphide at 170°, gives carbonyl sulphide, diphenylthiocarbamide, and phenylic thiocyanate, whilst methylic orthotolylimidotolylcarbamate gives ditolylthiocarbamide and tolylic thiocyanate on similar treatment; these two reactions are precisely similar to those which the amidines undergo when acted on by hydrogen sulphide and by carbon bisulphide respectively.

By the action of acetic chloride on ethylic phenylimidophenylcarbamate, diphenylcarbamide and acetodiphenylcarbamide are pro-

duced, whilst benzoic chloride gives diphenylcarbamide and *benzodiphenylcarbamide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NPh}\cdot\text{COPh}$ ; the latter is insoluble in water, but readily soluble in organic solvents, it crystallises in fine white needles, and melts at  $131^\circ$ ; when heated, it dissociates into benzanilide and phenylcarbimide.

The silver salt of dicarbethoxycarbamide, when acted on with ethylic iodide, gives *ethoxycarbonyldiurethane*,



this is a colourless, mobile oil, insoluble in water and dilute alkalis, and cannot be distilled at ordinary pressures, as it is completely decomposed. Dry hydrogen chloride acts on it at  $0^\circ$ , giving dicarbethoxycarbamide and ethylic chloride, and a similar change takes place slowly in presence of cold dilute hydrochloric acid. Alcoholic ammonia converts it very readily into dicarbethoxyguanidine. The sodium salt of dicarbethoxycarbamide appears to give only nitrogen ethers when treated with ethylic iodide.

T. M. L.

**Preparation of Alkylisocarbamides from Cyanamides.** By JULIUS STIEGLITZ and R. H. MCKEE (*Ber.*, 1899, 32, 1494—1496. Compare Abstr., 1894, i, 333, and Dains, preceding abstract).—When hydrogen chloride is led into an ice cold alcoholic solution of phenylcyanamide and the mixture left for two days, condensation occurs, and *ethylic imidophenylcarbamate (isophenylcarbamide)*,  $\text{NHPh}\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , is formed, and is isolated by pouring into 15 per cent. potassium hydroxide, extracting with ether, and dissolving the residue in light petroleum ( $40\text{--}60^\circ$ ); when purified by distillation under reduced pressure, it forms a colourless oil distilling at  $138\cdot5^\circ$  under 19 mm. pressure, and having a somewhat basic odour and a refractive index  $1\cdot5575$  at  $23^\circ$ ; it is readily soluble in most organic solvents, sparingly in cold water, yielding a solution with a strongly alkaline reaction. When decomposed with dry hydrogen chloride, it yields ethylic chloride and phenylcarbamide. The *platinochloride*,  $(\text{C}_9\text{H}_{12}\text{N}_2\text{O})_2\cdot\text{H}_2\text{PtCl}_6$ , has a deep yellow colour, and is sparingly soluble in alcohol or water.

J. J. S.

**Conversion of Phenylcarbamine and Phenylthiocarbimide into Acetanilide.** By BRONISLAW PAWLEWSKI (*Ber.*, 1899, 32, 1425—1426).—It is well known that phenylcarbamine and acetic acid yield formanilide and acetic anhydride. Acetanilide is obtained, however, when phenylcarbamine is heated with thiacetic acid until the mixture begins to boil. Thiacetic acid also reacts more readily with phenylthiocarbimide than acetic acid does (Werner, *Trans.*, 1891, 544); here also the main product, after boiling for half an hour, is acetanilide.

Dichloroacetic acid reacts readily with phenylcarbamine, forming dichloroacetanilide.

Some solubilities of acetanilide and of dichloroacetanilide are given in the paper.

C. F. B.

**Action of Aniline on Dithioacetylacetone.** By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1898, 19, [iii], 692—694. Compare Abstr., 1895, i, 168; 1896, i, 591; 1897, i, 265, and this vol., i, 415).—The

*phenylimide* of dithioacetylacetone,  $S_2(CHAc \cdot CMe : NPh)_2$ , is produced when this substance is heated with aniline (2 mols.) at  $100^\circ$ ; the crystals which slowly separate from the product are washed with ether to remove resinous impurities, and then dissolved in alcohol. The phenylimide separates from this solvent in small, yellow crystals which darken above  $120^\circ$  and melt at  $168^\circ$ . The *dihydrochloride*,  $C_{22}H_{24}N_2S_2O_2 \cdot 2HCl$ , crystallises in white spangles when hydrogen chloride is passed into a chloroform solution of the phenylimide, and is also produced by the action of sulphur chloride on the phenylimide of acetylacetone dissolved in chloroform; it sublimes readily, and is soluble in water.

Benzidine readily condenses with dithioacetylacetone when molecular proportions of these substances are heated on the water-bath; the condensation product which slowly separates from the mixture is washed with ether and crystallised from alcohol; analysis and a cryoscopic determination of the molecular weight indicate that the compound has the formula  $C_{22}H_{22}N_2S_2O_2$ ; it separates from its solutions in alcohol and chloroform as a golden-yellow, crystalline powder, which darkens and decomposes above  $150^\circ$ . G. T. M.

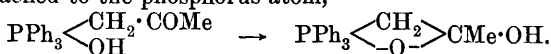
**$\epsilon$ -Amidocaproic Acid.** By SIEGMUND GABRIEL and THEODOR A. MAASS (*Ber.*, 1899, **32**, 1266—1272).— $\delta$ -Phenoxybutylamine (*Abstr.*, 1892, 131) was converted into  $\delta$ -phenoxybutylphthalimide, then into  $\delta$ -bromobutylphthalimide, this in its turn into ethylic phthalimidobutylmalonate, and finally into  $\epsilon$ -amidocaproic acid.

*$\delta$ -Phenoxybutylbenzamide*,  $OPh \cdot [CH_2]_4 \cdot NH \cdot COPh$ , the benzoyl derivative of  $\delta$ -phenoxybutylamine, crystallises from boiling light petroleum in glistening plates melting at  $72^\circ$ .

*$\delta$ -Phenoxybutylphthalimide*,  $OPh \cdot C_4H_8 \cdot N \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_4$ , formed when phthalic anhydride and  $\delta$ -phenoxybutylamine are heated together for some time at  $200^\circ$ , crystallises in colourless rhombic plates melting at  $101^\circ$ , and may be distilled under greatly reduced pressure without undergoing decomposition.  *$\delta$ -Bromobutylphthalimide* is best obtained by shaking the phenoxy-compound for 2 hours at  $100^\circ$  with an aqueous solution of hydrogen bromide saturated at  $0^\circ$ , and forms snow-white needles melting at  $80.5^\circ$ . *Ethylic phthalimidobutylmalonate*  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot C_4H_8 \cdot CH(COOEt)_2$ , is obtained as a colourless, thick oil when the bromo-compound is boiled for 2 hours with ethylic malonate, and a solution of sodium in absolute alcohol. When boiled with about four times its weight of hydrobromic acid of sp. gr. 1.49 for 2—3 hours, it is converted into phthalic acid and  $\epsilon$ -amidocaproic acid hydrobromide; this forms a fibrous, crystalline mass, which sinters at  $90^\circ$  and melts at  $105^\circ$ . The acid, obtained by the action of moist silver oxide on the hydrobromide, forms a crystalline powder which sinters at  $190^\circ$  and melts at  $202$ — $203^\circ$ . When carefully fused, gently heated until water is no longer given off, and then distilled under 10—15 mm. pressure, the lactam,  $CH_2 \begin{smallmatrix} \diagup CH_2 \cdot CH_2 \cdot CO \\ \diagdown CH_2 \cdot CH_2 \cdot NH \end{smallmatrix}$ , is obtained as an oil which solidifies to a mass of foliated crystals; it

is readily soluble in water, alcohol, ether, chloroform, or benzene, and crystallises from warm light petroleum in colourless plates melting at 65—69°, and consisting of the impure lactam. To purify the substance, it was converted into its aurichloride,  $(C_6H_{11}NO)_2HAuCl_4$ , which crystallises from warm water in prisms melting at 75—76°. Pyrrolidone and phthalimidine form analogously constituted aurichlorides. Although amidocaproic acid has no poisonous properties, the lactam is a nerve poison. J. J. S.

**A New Series of Betaines.** By AUGUST MICHAELIS and E. KÖHLER (*Ber.*, 1899, 32, 1566—1572).—Monochloracetone and monobromacetophenone combine with triphenylphosphine, forming compounds of the type  $PPh_3Cl \cdot CH_2 \cdot COMe$  and  $PPh_3Br \cdot CH_2 \cdot COPh$  respectively, which differ very considerably from simple phosphonium compounds, since the halogen atom is readily replaced by hydroxyl by means of alkali carbonates. These hydroxy-compounds are not deliquescent and alkaline like the phosphonium hydroxides with which they are probably isomeric, but are neutral, crystalline, and almost insoluble in water. Probably they are to be regarded as phosphorbetaines, formed by the wandering of the hydrogen of the hydroxyl group attached to the phosphorus atom,



On treatment with halogen acids, they pass into the original halogen salt.

*Triphenylmethylphosphorbetaine*,  $PPh_3 \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array} CMe \cdot OH$ , is precipitated from an aqueous solution of its hydrochloride on the addition of sodium hydroxide, or aqueous sodium carbonate, as a white, flocculent precipitate; it crystallises in glistening needles, melts at 201°, and behaves towards solvents in the same way as Michaelis and von Gimborn's triphenylphosphorbetaine. The *hydrochloride*,  $PPh_3Cl \cdot CH_2Ac$ , is prepared by heating a molecular mixture of triphenylphosphine and monochloracetone on the water bath for 45 minutes; it crystallises in slender needles which melt and partially decompose at 237°; the *platinochloride*,  $(C_{21}H_{20}PO)_2PtCl_6$ , crystallises in flesh-coloured leaflets melting and decomposing at 198°; the *hydrobromide* melts at 226°; the *picrate* forms lemon-yellow crystals and melts at 166°. *Tetraphenylphosphorbetaine*,  $PPh_3 \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array} CPh \cdot OH$ , formed in the same way from the hydrobromide, forms colourless crystals and melts at 183—184°; the *hydrobromide*, prepared from bromacetophenone and triphenylphosphine, melts at 273—274°, the *hydrochloride* crystallises in needles and melts at 254—255°, the *hydriodide* forms light, yellow needles and melts at 256—267°, and the *nitrate* forms colourless needles and melts at 184—185°.

*Triphenylparatolylphosphorbetaine*,  $PPh_3 \begin{array}{c} \diagup CH_2 \\ \diagdown O \end{array} C(C_7H_7) \cdot OH$ , prepared from the hydrochloride, crystallises in colourless, silky needles which melt at 181°. The *hydrochloride*, prepared from triphenylphosphine and chloroparatolyl methyl ketone, forms colourless needles melting at 231°, and is more soluble in water than the corresponding tetraphenyl derivative; the *platinochloride* forms reddish

yellow needles and melts and decomposes at  $211^{\circ}$ , the *hydrobromide* melts at  $261^{\circ}$ , the *hydriodide* at  $265^{\circ}$ , and the *nitrate* forms slender colourless crystals which melt at  $183$ — $184^{\circ}$ . J. F. T.

**Derivatives of Paratolualdehyde.** By WENZEL HANZLIK and AL. BIANCHI (*Ber.*, 1899, 32, 1285—1289).—Paratolualdehyde has a sp. gr. 1.072 at  $12^{\circ}$ , and a refractive index for sodium light 1.5484 at  $14^{\circ}$ ; its sodium hydrogen sulphite compound consists of white, glistening plates readily soluble in water and sparingly soluble in alcohol or ether; its *phenylhydrazone* forms light yellow crystals melting at  $108^{\circ}$ , and the *parasulphophenylhydrazone* light yellow prisms melting at  $270$ — $271^{\circ}$ .

*Diparatoluylidenehydrazone* (paratolylazine),  $N_2:(CH \cdot C_6H_4Me)_2$ , prepared from the aldehyde and hydrazine, crystallises in lemon-yellow, rhombic prisms melting at  $154$ — $155^{\circ}$ .

The compound of the aldehyde with *orthonitrophenylhydrazine* separates from dilute alcohol in red needles which melt at  $181^{\circ}$ , whilst the corresponding *paranitro*-derivative forms dark-red needles melting at  $196^{\circ}$ .

The *orthonitroparasulphophenylhydrazone* is an orange dye which is readily soluble in water and melts at  $195^{\circ}$ .

*Paratoluylidene metanitrilaniline* forms brownish-yellow crystals melting at  $79^{\circ}$ , and the *para*-derivative crystallises from acetone in long, yellow needles melting at  $135^{\circ}$ .

*Paratoluylidene metanitrometaxylidine* separates from its alcoholic solution in yellow, monoclinic plates melting at  $145^{\circ}$ , the corresponding *metanitroparaxylidine* forming light yellow prisms melting at  $110^{\circ}$ .

The *leuco*-base of *paramethylmalachite-green*,  $C_6H_7Me \cdot CH(C_6H_4 \cdot NMe_2)_2$ , formed by the condensation of the aldehyde with excess of dimethylaniline in the presence of zinc chloride, crystallises in small needles which melt at  $93$ — $94^{\circ}$ ; its oxidation to the colour base, which closely resembles ordinary malachite-green in appearance and properties, is readily brought about by either chloranil in alcoholic solution, or by lead peroxide.

*Metanitroparatolualdehyde* is readily obtained by the nitration of paratolualdehyde, and crystallises from ether in long needles melting at  $43$ — $44^{\circ}$ ; the *phenylhydrazone* forms orange-coloured crystals melting at  $112^{\circ}$ ; the *paranitrophenylhydrazone* is a reddish-brown, crystalline powder melting at  $223$ — $224^{\circ}$ , and the *orthonitroparasulphophenylhydrazone* an orange wool-dye melting at  $200$ — $202^{\circ}$ .

*Dimetanitroparatoluylidenehydrazone* is a light yellow, crystalline powder which melts at  $184$ — $185^{\circ}$ , and *metanitroparatoluylidene metanitrilaniline* separates from alcohol in light yellow needles melting at  $156^{\circ}$ . J. F. T.

**Iodine Substitution Products of some Aromatic Alcohols, Aldehydes, and Acids.** By JOHANNES SEIDEL (*J. pr. Chem.*, 1899, [ii], 59, 105—149).—The main portion of this paper deals with the iodination of saligenin, salicylaldehyde, parahydroxybenzaldehyde, and anisaldehyde, which has previously been described (*Abstr.*, 1898, i, 367, 663). Attempts have been made to iodinate coumarin directly, the best results being obtained by a modification of Kekulé and

Körner's methods (Kekulé, *Annalen*, 1864, 131, 221; Körner, *ibid.*, 1866, 137, 213). An alkaline solution of coumarin was saturated with carbonic anhydride, cooled, and the calculated quantity of iodine added; the product obtained was probably iodocoumaric acid,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$ , a white powder melting at about  $203^\circ$ .

The results show that, contrary to Kekulé's theory, iodination can be effected in the case of substances having a pronounced phenolic character in the absence of an agent to combine with the hydrogen iodide formed; in other cases, however, the reaction must be carried out under pressure, and at a high temperature in the presence of iodic acid or a similar substance.

F. H. N.

**Elimination of Substituting Groups from the Benzene Ring. I. Behaviour of the Acyl and Carboxyl Groups.** By AUGUST KLAGES and G. LICKROTH (*Ber.*, 1899, 32, 1549—1565).—The formation of the double compounds of phosphoric acid with aromatic ketones described by Klages and Allendorff (*Abstr.*, 1898, i, 477) is affected by the entrance of alkyl groups into the ring, depending however, not on the number or nature of such groups, but on the positions occupied by them. Thus these compounds are not formed when the ketone group is attached to the benzene ring in the ortho-position to two alkyl groups, acetylmesitylene not giving any compound, whilst acetylpsudocumene readily gives one. The behaviour of diacetylmetaxylylene is interesting; this compound, which contains one acetyl group in the ortho-position to two alkyl groups and the other in the ortho-position to one, should combine with only one molecule of phosphoric acid, which, as a matter of fact, it does, whereas diacetylbenzene combines with two mols. of the acid.

The behaviour of fatty aromatic ketones when boiled with phosphoric acid is also dependent on the position of the alkyl groups in the aromatic ring; compounds of the type  $\text{Ph}\cdot\text{CO}\cdot\text{R}$ , and compounds in which an alkyl group is substituted in the para- or meta-position to the acyl group remain unchanged, whilst when the alkyl group is in the ortho-position, about 20—30 per cent. of the compound is hydrolysed after boiling for 8 hours, and when the acyl group is in the ortho-position to two alkyl groups, complete hydrolysis ensues after heating for half an hour. This hydrolysis by means of phosphoric acid differs from that brought about by potassium hydroxide as disruption of the chain takes place, not between the alkyl group and the carbonyl, but between the carbonyl and the aromatic ring, forming a fatty acid and an aromatic hydrocarbon; thus, from diacetylmesitylene, diacetyldurene and diacetylisodurene, a quantitative yield of mesitylene, durene and isodurene respectively can be obtained. This action of phosphoric acid and the conditions which regulate it apply, not only to fatty aromatic ketones, but also to compounds in which the ketonic group is attached to radicles other than alkyl; thus mesitylenecarboxylic acid is quantitatively resolved into mesitylene and carbonic anhydride, durenecarboxylic acid behaving similarly, whilst prehnitene-carboxylic acid, under the same conditions, remains unchanged. In this reaction, hydrochloric acid, or, better still, hydriodic acid (b. p.  $127^\circ$ ) may be substituted for phosphoric acid.



Ketones of the benzophenone group are only slowly hydrolysed by phosphoric acid. Thus benzoylmetaxylene yields 20 per cent. of the hydrocarbon after boiling for 8 hours and benzoylmesitylene and benzoyltriethylbenzene, 30 per cent. in the same time.

The phosphoric acid compound of acetophenone is decomposed in ethereal solution by aniline forming *aniline phosphate*, which crystallises from alcohol in glistening needles and melts at 180°. The *double compound* of arsenic acid and acetophenone crystallises from alcohol and melts sharply at 97°; it does not appear, however, to be a homogeneous substance.

*Paracetyltoluene* distils at 116° under 23 mm. and at 219° under ordinary pressure; its compound with phosphoric acid melts at 90°.

*Paracetyلهthylbenzene* boils at 130° under 23 mm. and at 236° under ordinary pressure, and has a sp. gr. 0.991 at 20°/4°; its phosphoric acid compound, which is deliquescent, melts at about 30°.

*Parapropionylethylbenzene* is a colourless, mobile liquid of intensely sweet taste, which boils at 246° and has a sp. gr. 0.986 at 18°/4°. The *oxime* forms large, rhombic plates and melts at 58—59°. The ethers of oxyketones also combine with phosphoric acid; thus the compound with *paracetylanisole* melts at 86°, and that with *paracetylphenetole* at 81°. *Parapropionylanisole* does not combine with phosphoric acid, but on boiling with it is partially hydrolysed into *anisole*. All these ketones were prepared from the aromatic hydrocarbons and the fatty acid chlorides by Friedel and Craft's reaction, but the following were prepared by Freund's method from the aromatic acid chloride and zinc methyl:

*Metatoluic chloride* is a colourless oil which distils at 120° under 38 mm. pressure and has a sp. gr. 1.173 at 20°/4°. *Metacetyltoluene* boils at 220° and has a sp. gr. 0.986 at 20°/4°.

*Orthotoluic chloride* boils at 100—102° under 21 mm. pressure, and with zinc methyl is converted into *orthacetyltoluene*, which boils at 213° (216° corr.) and has a sp. gr. 1.026 at 20°/4°.

*Propionylpseudocumene*,  $C_6H_5Me_3 \cdot COEt$  [= 1 : 3 : 4 : 5], prepared from pseudocumene, propionic chloride, and aluminium chloride, boils at 154° under 29 mm., or at 257° under ordinary pressure, has a sp. gr. 0.985 at 18°/4°, and forms a compound with phosphoric acid which melts at 87°.

*Propionylpentethylethylbenzene*, prepared by Friedel and Craft's reaction, melts at 70—71° and boils at 179—180° under 19 mm. pressure.

*Symmetrical trimethyldeoxybenzoin*,  $C_6H_5Me_3 \cdot CO \cdot CH_2Ph$ , is at first obtained as a light yellow oil of sp. gr. 1.046 at 18°/4° which distils at 204° under 21 mm. pressure; it solidifies after some time and then forms colourless needles melting below 30°.

*Triethylbenzophenone* is a yellow oil of sp. gr. 1.032 at 20°/4° which boils at 210—220° under 40 mm. or at 340° under ordinary pressure.

J. F. T.

**Action of Sulphur Chloride on the Copper Derivative of Benzoylacetone.** By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1898, [iii], 19, 833—837).—It was shown in a previous paper (*Abstr.*, 1895, i, 168) that the copper derivative of benzoylacetone reacts with

sulphur chloride in chloroform solution to form dithiobenzoylacetone,  $S_2(CHAcBz)_2$ ; this substance, which has now been obtained in considerable quantity, forms pale yellow, rhombic crystals, has a slight aromatic odour, is optically active, melts at  $117-118^\circ$ , is insoluble in water, but more or less soluble in organic solvents, and gives a reddish-violet coloration with ferric chloride. The *sodium* derivative,  $C_{20}H_{16}Na_2S_2O_4$ , obtained by the action of sodium or, more readily, of sodium ethoxide on dithiobenzoylacetone in ethereal solution, is a yellow, crystalline compound which is very soluble in water, less soluble in alcohol, and insoluble in ether. The *copper* derivative,  $C_{20}H_{16}CuS_2O_4$ , obtained as a dark green, amorphous powder when an ethereal solution of dithiobenzoylacetone is added to a dilute alcoholic solution of cupric acetate, is insoluble in water, but soluble in ether or chloroform, and soon turns brown and decomposes at the ordinary temperature. The *ferric* derivative,  $Fe_2(C_{20}H_{16}S_2O_4)_3$ , obtained from the sodium compound by double decomposition, is a brick-red, amorphous powder, insoluble in water, slightly soluble in alcohol, and more soluble in chloroform. A canary-yellow, crystalline compound of the composition  $C_{20}H_{18}S_2O_4 \cdot 2NH_3$  is produced when a current of dry ammonia gas is passed into an ethereal solution of dithiobenzoylacetone, or when the latter is mixed with a saturated alcoholic solution of ammonia. It is very soluble in water, fairly soluble in alcohol, and rapidly decomposes on exposure to air, with evolution of ammonia. This decomposition is immediately brought about by dilute acids.

N. L.

**Synthesis of Di-substituted Acetic Acids by means of Chloral.** By PAUL FRITSCH and FELIX FELDMANN (*Annalen*, 1899, 306, 72—86. Compare Abstr., 1898, i, 63).—The products of condensing chloral with benzene, toluene, and anisole have been already described. *Diphenetyltrichlorethane*,  $CCl_3 \cdot CH(C_6H_4 \cdot OEt)_2$ , prepared by adding concentrated sulphuric acid to a solution of phenetol and chloral hydrate in glacial acetic acid, crystallises in lustrous prisms, and melts at  $105^\circ$ .

Alcoholic potash converts derivatives of trichlorethane into the corresponding dichlorethylenes; diphenyldichlorethylene and ditolyldichlorethylene have been already described. *Dianisylldichlorethylene*,  $CCl_2 \cdot C(C_6H_4 \cdot OMe)_2$ , crystallises in stout, prismatic needles and melts at  $113^\circ$ ; *diphenetyldichlorethylene*,  $CCl_2 \cdot C(C_6H_4 \cdot OEt)_2$ , melts at  $106.5^\circ$ .

When heated with alcoholic sodium ethoxide in sealed tubes at  $180^\circ$ , the dichlorethylene derivatives yield di-substituted acetic acids, associated in the case of ditolyldichlorethylene and diphenetyldichlorethylene with dimethyltolane and diethoxytolane respectively. *Ditolylacetic acid*,  $COOH \cdot CH(C_6H_4Me)_2$ , crystallises from glacial acetic acid in needles and melts at  $144^\circ$ . The *methylic* and *ethylic* salts melt at  $36-37^\circ$  and  $65^\circ$  respectively, whilst the *ammonium* salt crystallises in slender needles and rapidly loses ammonia at  $100^\circ$ ; the *barium* and *calcium* salts contain  $2H_2O$ .

*Dianisylacetic acid*,  $COOH \cdot CH(C_6H_4 \cdot OMe)_2$ , forms lustrous needles melting at  $110^\circ$ . The *methylic* salt crystallises in lustrous plates and melts at  $66-67^\circ$ ; the *barium* and *calcium* salts

crystallise in small needles containing  $2\text{H}_2\text{O}$ . *Diphenetylacetic acid*,  $\text{COOH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$ , melts at  $114^\circ$ ; the *methylic* and *ethylic* salts melt at  $68^\circ$  and  $47^\circ$  respectively, whilst the *barium* and *calcium* salts crystallise in small needles containing  $2\text{H}_2\text{O}$ .

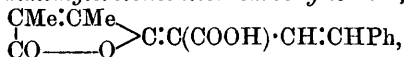
The constitution of the di-substituted acetic acids has been established by oxidising them to the corresponding ketones. M. O. F.

**Condensation of Phenylisocrotonic Acid with Pyrocinchonic Anhydride.** By JOHANNES THIELE (*Annalen*, 1899, 306, 240—246).—*Cinnamylidenedimethylcrotonolactone* (7-phenyl-2:3-

*dimethylheptatrieneolide*-1:4),  $\begin{array}{c} \text{CMe}\cdot\text{CMe} \\ | \quad \diagup \\ \text{CO} \text{---} \text{O} \end{array} > \text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHPh}$ , prepared

by heating sodium phenylisocrotonate with pyrocinchonic anhydride at  $150^\circ$  and treating the product with acetic anhydride, crystallises from alcohol in small, yellow needles and melts at  $153^\circ$ ; the solution in concentrated sulphuric acid is orange-red, and alcoholic potash develops a yellow coloration which becomes dark brown on exposure to air. An alkaline solution of the lactone forms an intense red liquid with diazobenzenesulphonic acid or with diazobenzene, as in the case of a phenol.

*Cinnamylidenedimethylcrotonolactonecarboxylic acid*,



the initial product of condensing phenylisocrotonic acid with pyrocinchonic anhydride, crystallises from alcohol in small, yellow needles, and melts at  $216^\circ$ .

When cinnamylidenedimethylcrotonolactone is heated with alcoholic ammonia at  $125\text{--}130^\circ$  during 4 hours, the additive compound,  $\text{C}_{15}\text{H}_{17}\text{NO}_2$ , is obtained, crystallising in white leaflets containing  $1\text{H}_2\text{O}$  and melting at  $113^\circ$ ; the anhydrous substance melts at  $142^\circ$ . Mineral acids convert it into the *imide*,  $\text{C}_{15}\text{H}_{15}\text{NO}$ , which consequently forms the chief product of the action of alcoholic ammonia on cinnamylidenedimethylcrotonolactone; it crystallises from glacial acetic acid in small, yellow needles, and melts indefinitely at  $248^\circ$ .

M. O. F.

**Formation of a Hydroxylactone by the Condensation of Benzaldehyde and Pyruvic Acid.** By EMIL ERLÉNMEYER, jun., (*Ber.*, 1899, 32, 1450—1455. Compare *Abstr.*, 1894, i, 592).—The condensation of benzaldehyde and pyruvic acid has already been studied by Claisen and Claparède (*Abstr.*, 1882, 520), who obtained as chief product cinnamylformic acid; working under exactly the same conditions, the author has obtained, in addition, two crystalline derivatives. One

of these,  $\gamma$ -phenyl- $\beta$ -benzylidene- $\alpha$ -ketobutyrolactone.  $\text{CO} < \begin{array}{c} \text{O} \text{---} \text{CHPh} \\ \diagdown \quad | \\ \text{CO} \cdot \text{C} \cdot \text{CHPh} \end{array}$ , is formed in only minute quantities under the conditions employed by Claisen and Claparède, but a good yield may be obtained by saturating a mixture of benzaldehyde (2 mols.) and pyruvic acid (1 mol.) at low temperatures with dry hydrogen chloride and keeping the mixture for 3 days at the ordinary temperature, then extracting with water, and precipitating from the aqueous solution with ether; it

crystallises in well-defined, yellow prisms melting at  $167^{\circ}$ , and combines with bromine yielding a *dibromide* which crystallises in colourless needles melting at  $135^{\circ}$ , but another product melting at  $209^{\circ}$  is also formed, and part of the lactone remains unchanged. The lactone has neutral properties, but dissolves in alkalis, yielding salts of  $\gamma$ -hydroxy- $\gamma$ -phenyl- $\beta$ -benzylidene- $\alpha$ -ketobutyric acid,



The *sodium* salt, with  $4\text{H}_2\text{O}$ , crystallises in colourless, flat needles; the *barium* and *silver* salts were also prepared. When the lactone is warmed with sodium hydroxide solution, benzaldehyde is formed, and when oxidised with dilute nitric acid, benzoic acid is the chief product; with alkaline permanganate, oxalic acid is formed. J. J. S.

**Ethyllic Trinitrophenylmalonate.** By C. LORING JACKSON and J. I. PHINNEY (*Amer. Chem. J.*, 1899, 21, 418—433).—Ethyllic trinitrophenylmalonate, which was originally obtained in long, white, slender plates melting at  $58^{\circ}$  (Abstr., 1896, i, 234, 370), has been obtained in a new form by acidifying a solution of the ammonium salt; it then crystallises in four (or six)-sided plates, in which two opposite angles are unlike, one being acute and the other obtuse, and melts at  $64^{\circ}$ . Since the discovery of this form, it has always been obtained to the entire exclusion of the other, and even when specimens of the first modification have been recrystallised, they have undergone conversion into the second; this behaviour is doubtless due to the dissemination of particles of the stable modification through the building in which the experiments have been conducted, as it is found that the minutest trace is sufficient to convert the form of low melting point in saturated solution into that of high melting point.

It is believed that the difference between the two forms is due to the same cause as that existing between the two forms of ethyllic anilidotrinitrophenyltartronate (Jackson and Bentley, Abstr., 1892, 1217), and that the difference is of a chemical, and not of a purely physical, nature appears certain from the fact that both have been converted into salts and recovered unchanged on acidification. It is suggested that possibly one contains the enolic and the other the ketonic form of the malonic residue. The new modification is white, but gives dark-red salts; the *ammonium* salt is composed of rich golden-brown, hair-like needles, decomposes below  $100^{\circ}$ , and afterwards melts to a yellowish-brown liquid, which explodes at higher temperatures. An aqueous solution of the ammonium salt gives red precipitates with salts of strontium, calcium, zinc, cadmium, copper, and lead, and a crystalline, amethyst-coloured precipitate with barium salts.

When nitric acid acts on ethyllic trinitrophenylmalonate, the *nitrite*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{C}(\text{COOEt})_2 \cdot \text{O} \cdot \text{NO}$ , of the corresponding ethyllic trinitrophenyltartronate is obtained, which crystallises in long, flat, white prisms, belonging apparently to the monoclinic system, melts and decomposes at  $109^{\circ}$ , dissolves readily in ethylic and methylic alcohols, chloroform, ether, benzene, acetic acid, or acetone, is nearly insoluble in carbon bisulphide and in cold water, but dissolves sparingly in hot water, giving a pink solution. Cold mineral acids

have no effect on the substance, which is decomposed by hot sulphuric acid, however, and is converted into the corresponding ethylic tartrate by hot nitric acid; it is gradually dissolved by alkalis, giving red solutions.

*Ethylic trinitrophenyltartrate*,  $C_6H_2(NO_2)_3 \cdot C(COOEt)_2 \cdot OH$ , forms aggregates of white, fluffy needles, melts at  $117^\circ$ , dissolves readily in ethylic and methylic alcohols, ether, benzene, chloroform, or acetone, is soluble in glacial acetic acid, somewhat soluble in carbon bisulphide, and sparingly so in light petroleum. It is decomposed by hot sulphuric acid, gas being evolved, and appears to be hydrolysed by alkalis. The *acetyl* derivative forms white, flat, probably monoclinic prisms. The *benzoyl* derivative forms white crystals melting at  $152^\circ$ .

*Trinitrophenylacetic acid*,  $C_6H_2(NO_2)_3 \cdot CH_2 \cdot COOH$ , made by boiling ethylic trinitrophenylmalonate with sulphuric acid of sp. gr. 1.44 for some hours, crystallises from benzene in short needles melting at  $161^\circ$ ; it is converted into the corresponding trinitrotoluene (m. p.  $81^\circ$ ) when warmed with alcohol or water. It dissolves readily in ether, glacial acetic acid, acetone, or light petroleum, is soluble in chloroform, and less so in benzene or carbon bisulphide.

Attempts to prepare ethylic ditritrophenylmalonate have proved unsuccessful. A. L.

**Addition of Hydrogen Cyanide to Ethylic Cinnamylidenemalonate.** By JOHANNES THIELE and JAKOB MEISENHEIMER (*Annalen*, 1899, 306, 247—266. Compare Bredt and Kallen, *Abstr.*, 1897, i, 154).—Cinnamylidenemalonate acid has been described by Liebermann (*Abstr.*, 1895, i, 470); the *methylic* and *ethylic* salts melt at  $67^\circ$  and  $36^\circ$  respectively.

*Cinnamenylsuccinic acid*,  $CHPh:CH:CH(COOH) \cdot CH_2 \cdot COOH$ , prepared by heating an alcoholic solution of ethylic cinnamylidenemalonate with potassium cyanide and hydrolysing the nitrile with 5 per cent. caustic potash, separates from dilute alcohol in prismatic crystals and melts at  $173^\circ$ . The *anhydride* melts at  $116^\circ$ .

*Benzylparaconic acid*,  $CO \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CH} \cdot \text{CH}_2 \text{Ph} \end{array}$ , obtained from cinnamenylsuccinic acid by the action of hydrogen bromide in glacial acetic acid, crystallises in white prisms and melts at  $93^\circ$ .

*Phenethylsuccinic acid*,  $CH_2Ph:CH:CH(COOH) \cdot CH_2 \cdot COOH$ , prepared by heating cinnamenylsuccinic acid with hydriodic acid and red phosphorus, is also produced by hydrolysing the nitrile from ethylic phenylpropylidenemalonate (see below) and hydrogen cyanide; it crystallises from benzene and melts at  $136^\circ$ . The *anhydride* melts at  $56^\circ$ ; the *paratolilic acid* crystallises in colourless needles melting at  $146^\circ$  and yields the *hydrogen ammonium* salt in leaflets which melt and evolve gas at  $185^\circ$ .

*Phenylpropenylmalonic* (1:4-hydrocinnamylidenemalonate) *acid*,  $CH_2Ph:CH:CH(COOH)_2$ , formed when cinnamylidenemalonate acid is reduced in alkaline solution with sodium amalgam, crystallises from benzene in white leaflets which melt and decompose at  $106$ — $108^\circ$ ; the *sodium* salt is anhydrous, and the *barium* salt contains  $1H_2O$ .

*Phenylpropylidenemalonate* (3:4-hydrocinnamylidenemalonate) *acid*,

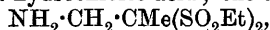
$\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{COOH})_2$ , obtained from the foregoing acid by protracted treatment with caustic soda on the water-bath, melts and decomposes at  $115-116^\circ$ ; the *barium* salt contains  $1\text{H}_2\text{O}$ .

*Phenylbutanetricarboxylic acid*,  $\text{C}_4\text{H}_5\text{Ph}(\text{COOH})_3$ , prepared by hydrolysing the nitrile from ethylic cinnamylidenemalonate and potassium cyanide, melts indefinitely at  $180-185^\circ$ ; the *methylic* salt crystallises in large prisms melting at  $46^\circ$ , and boils at  $328-336^\circ$  under 718 mm. pressure. The *anhydride* crystallises from benzene in leaflets and melts at  $112^\circ$ .  
M. O. F.

**Action of Sulphuric Acid on Thymol.** By JAMES H. STEBBINS (*J. Amer. Chem. Soc.*, 1899, 21, 276—281. Compare *ibid.*, 1881, 3, 103—110).—The chief product of the sulphonation of thymol with sulphuric acid of sp. gr. 1.83 at  $100^\circ$  is the para-acid  $[\text{Me}:\text{SO}_3\text{H}:\text{Pr}:\text{OH} = 1:2:4:5]$ ; its constitution has been established by Claus (Abstr., 1899, 899), and is also shown by the formation of the thymoquinone melting at  $45.5^\circ$  when oxidised with chromic acid. The ortho-acid  $[\text{Me}:\text{SO}_3\text{H}:\text{C}_3\text{H}_7:\text{OH} = 1:2:4:3]$  does not appear to be produced, but a small quantity of a disulphonic acid was separated. T. M. L.

**Disulphones. I. Nitrogen Derivatives of Sulphonal.** By THEODOR POSNER (*Ber.*, 1899, 32, 1239—1251).—Gabriel and Posner (Abstr., 1894, i, 355) have shown that amidoacetone-ethylmercaptole cannot be obtained by the action of hydrochloric acid on phthalimidoacetone-ethylmercaptole, as the reaction proceeds further and phthalic acid, ethylmercaptan, and amidoacetone hydrochloride are the final products. Amidosulphonal may, however, be prepared by a different method. *Phthalimidodisulphonal* (*phthalimidoacetonedietiylidisulphone*),  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{N}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2$ , is obtained when phthalimidoacetone-ethylmercaptole is carefully dissolved in cold acetic acid and then oxidised with an excess of a cold saturated solution of potassium permanganate; it forms large, lustrous, colourless plates, melts at  $175-177^\circ$  (corr.), is practically insoluble in water, but dissolves readily in alcohol or acetic acid.

When treated with strong potassium hydroxide solution, a heavy oil consisting of *potassium sulphonalphthalamate* is formed, which is readily soluble in water, and when warmed with hydrochloric acid yields *sulphonalphthalamic acid*,  $\text{CMe}(\text{SO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , which, when boiled with concentrated hydrochloric acid, is hydrolysed to phthalic acid and *amidosulphonal hydrochloride*; a better yield of the latter is obtained when phthalimidodisulphonal is heated for 3 hours at  $170^\circ$  with concentrated hydrochloric acid; the *base* itself,

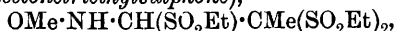


may be obtained by treatment with an excess of alkali and repeated extraction with ether; it crystallises in short, monoclinic prisms melting at  $94-96^\circ$  (corr.), is moderately soluble in cold, readily in hot water and also in most organic solvents with the exception of light petroleum. The *hydrochloride* crystallises from alcohol in small, colourless needles, or in well-developed, rhombic plates melting at  $190-191^\circ$  (corr.); the *platinochloride* crystallises in orange-yellow

prisms melting and decomposing at  $225^{\circ}$ , the *picrate* is sparingly soluble in water, but the *sulphate*, *nitrate*, and *oxalate* are readily soluble. When a hydrochloric acid solution of the base is treated with sodium nitrite, a small quantity of a substance melting at  $71-75^{\circ}$  is obtained; whether this is hydroxysulphonol has not been determined.

*Nitrosoacetone-ethylmercaptole*,  $\text{NO}\cdot\text{CH}_2\cdot\text{CMe}(\text{SEt})_2$ , is obtained when an ethereal solution of isonitrosoacetone and ethylmercaptan is saturated in the cold with dry hydrogen chloride and left until the ether has evaporated; it is a yellowish-red oil, and is so readily decomposed that it cannot be purified. When the chloroform solution is mixed with acetic acid and oxidised with an excess of potassium permanganate, *nitrososulphonol*,  $\text{NO}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2$  is obtained, which crystallises from alcohol in well-developed, six-sided rhombic plates melting at  $104-105^{\circ}$  (corr.).

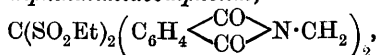
Isonitrosomethylacetone (Ceresole, *Ber.*, 1883, 16, 833) also condenses with mercaptan in the presence of hydrogen chloride, and the product when oxidised gives *methoxyamidopropane- $\alpha\beta$ -triethylsulphone* (*isonitrosomethylacetone-triethylsulphone*),



and is therefore probably methoxyamido- $\alpha\beta$ -trithioethylpropane,  $\text{OMe}\cdot\text{NH}\cdot\text{CH}(\text{SEt})\cdot\text{CMe}(\text{SEt})_2$ , formed by the direct union of ethylmercaptan with isonitrosomethylacetone-ethylmercaptole; the trisulphone crystallises in colourless plates and melts at  $72^{\circ}$  (corr.). Ethylisonitrosoacetone, boiling at  $130^{\circ}$ , when treated in a similar manner, yields a reddish oil which, on oxidation, gives *isonitrosoethylacetone-triethyltrisulphone*,  $\text{OEt}\cdot\text{NH}\cdot\text{CH}(\text{SO}_2\text{Et})\text{CMe}(\text{SO}_2\text{Et})_2$ ; it crystallises in long, colourless prisms, is readily soluble in hot ethylic acetate or alcohol, and is very stable, being only partially decomposed when heated for 2 hours at  $200^{\circ}$  with concentrated hydrochloric acid. The yields of isonitrosoethylacetone and of its trisulphone derivative are much better than in the case of the methylic compounds.

Ethylic nitrosoacetoacetate also condenses with ethylmercaptan, but the product, when oxidised, does not yield a crystalline sulphone.

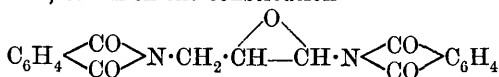
The condensation of diphthalimidoacetone (Abstr., 1894, i, 355) with mercaptan does not take place at all readily, on account of the slight solubility of the acetone derivative in most solvents; it is most easily effected by using an acetic acid solution saturated in the cold with hydrogen chloride, and heating with the mercaptan for several hours in sealed tubes at  $60-70^{\circ}$ ; the *diphthalimidacetone-ethylmercaptole*,  $\text{C}(\text{SEt})_2\left(\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\right\rangle\text{N}\cdot\text{CH}_2\right)_2$ , is precipitated by the addition of water, and forms a white powder melting at  $176-177^{\circ}$ ; when oxidised, it yields *diphthalimidodisulphonol*,



melting at  $218-220^{\circ}$ .

The product obtained by Hörmann (Abstr., 1881, 248) by oxidising symmetrical dichlorhydrin is not dichloracetone but pseudodichloracetone, since, when heated with potassium phthalimide, it does not

yield diphthalimidoacetone melting at  $268^{\circ}$ , but an isomeric compound melting at  $220^{\circ}$ , to which the constitution



is ascribed.

J. J. S.

**Iodoso- and Iodoxy-compounds of Di-iododiphenylsulphone.** By CONRAD WILLGERODT and O. WALDEYER (*J. pr. Chem.*, 1899, [ii], 59, 194—197. Compare Langmuir (Abstr., 1895, i, 230).—*Iodiodosodiphenylsulphone*,  $\text{C}_6\text{H}_4 \cdot \text{I} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{IO}$ , a bright yellow, amorphous powder decomposing at  $184^{\circ}$ , was obtained from di-iododiphenylsulphone by converting it into iododiphenyl iodochloride by means of chlorine, and treating this with dilute sodium hydroxide.

*Di-iodoxydiphenylsulphone*,  $\text{SO}_2(\text{C}_6\text{H}_4 \cdot \text{IO}_2)_2$ , was obtained as a very sparingly soluble, colourless substance exploding at  $212^{\circ}$  by oxidising the iodiodoso-compound with hypochlorous acid.

Attempts to prepare periodosobenzenesulphonic acid were unsuccessful.

F. H. N.

**Sulphonated Butyric Acids.** By JULIUS TROEGER and ROBERT UHDE (*J. pr. Chem.*, 1899, [ii], 59, 320—349. Compare Otto (Abstr., 1890, 379, &c.).—*Ethylic phenylsulphonebutyrate*,  $\text{SO}_2\text{Ph} \cdot \text{CHEt} \cdot \text{COOEt}$ , made by heating sodium benzenesulphinate and ethylic  $\alpha$ -bromobutyrate in alcoholic solution for 30 hours on the water-bath, crystallises from alcohol in shining, prismatic forms melting at  $60$ — $61^{\circ}$ , and is soluble in alcohol, ether, and acetic acid, but insoluble in water. The acid,  $\text{SO}_2\text{Ph} \cdot \text{CHEt} \cdot \text{COOH}$ , which has already been obtained in small quantity by Otto (*loc. cit.*), dissolves in alcohol, ether, acetic acid, or hot water, and melts at  $123$ — $124^{\circ}$ . The sodium salt cannot be dried on the water-bath, and loses carbonic anhydride at  $110^{\circ}$ . The barium salt,  $(\text{C}_{10}\text{H}_{11}\text{SO}_4)_2\text{Ba}$ , and the calcium salt,  $(\text{C}_{10}\text{H}_{11}\text{SO}_4)_2\text{Ca}$ , form glassy masses. The silver salt,  $(\text{C}_{10}\text{H}_{11}\text{SO}_4)\text{Ag}$ , crystallises in fine leaflets from hot water.

*Ethylic paratolylsulphonebutyrate*,  $\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{CHEt} \cdot \text{COOEt}$ , crystallises in slender needles, melts at  $42^{\circ}$ , and is insoluble in water, but dissolves in alcohol, ether, acetic acid, or ethylic acetate. The acid sinters at  $42^{\circ}$  and melts at  $47^{\circ}$ . The sodium salt,  $(\text{C}_{11}\text{H}_{13}\text{SO}_4\text{Na})$ , is a syrupy mass which cannot be dried. The barium salt,  $(\text{C}_{11}\text{H}_{13}\text{SO}_4)_2\text{Ba} + \text{H}_2\text{O}$ , forms microscopic needles. The silver salt,  $\text{C}_{11}\text{H}_{13}\text{SO}_4\text{Ag}$ , forms small leaflets.

*Ethylic  $\alpha$ -naphthylsulphonebutyrate*,  $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{CHEt} \cdot \text{COOEt}$ , crystallises in shining, granular crystals which melt at  $71$ — $72^{\circ}$ . The acid forms a crystalline powder, melts at  $82^{\circ}$ , and dissolves in alcohol, ether, acetic acid, and ethylic acetate, but is only sparingly soluble in hot water. The sodium salt is syrupy. The barium salt,  $(\text{C}_{14}\text{H}_{13}\text{SO}_4)_2\text{Ba} + 3\text{H}_2\text{O}$ , forms crystals which readily effloresce.

*Ethylic  $\beta$ -naphthylsulphonebutyrate*,  $\text{C}_{16}\text{H}_{13}\text{SO}_4$ , crystallises from dilute alcohol in slender needles and melts at  $63$ — $64^{\circ}$ . The acid,  $\text{C}_{14}\text{H}_{11}\text{SO}_4 + \text{H}_2\text{O}$ , crystallises from dilute alcohol in slender, white needles



melting at  $110^{\circ}$ , and dissolves in alcohol, ether, acetic acid, ethylic acetate, and much hot water. The *sodium* salt is syrupy. The *barium* salt,  $(C_{14}H_{13}SO_4)_2Ba + 3H_2O$ , forms microscopic prisms.

*Ethylic phenylsulphonisobutyrate*,  $SO_2Ph \cdot CMe_2 \cdot COOEt$ , forms white crystals and melts at  $38-39^{\circ}$ . The *acid* is much more difficult to prepare by the hydrolysis of the ethylic salt than is the corresponding normal acid. The *sodium* salt,  $C_{10}H_{11}SO_4Na + 3H_2O$ , separates from hot aqueous solution in slender, transparent needles. The *barium* salt,  $(C_{10}H_{11}SO_4)_2Ba$ , forms fine, white leaflets.

*Ethylic paratolylsulphonisobutyrate*,  $C_7H_7 \cdot SO_2 \cdot CMe_2 \cdot COOEt$ , forms light yellow crystals and melts at  $79-80^{\circ}$ . The *acid* forms white crystals, melts at  $124-125^{\circ}$ , and is soluble in alcohol, ether, ethylic acetate, or hot water. The *sodium* salt,  $C_{11}H_{13}SO_4Na$ , crystallises in microscopic prisms. The *barium* salt,  $(C_{11}H_{13}SO_4)_2Ba$ , crystallises in slender, felted needles.

*Ethylic  $\alpha$ -naphthylsulphonisobutyrate*,  $C_{10}H_7 \cdot SO_2 \cdot CMe_2 \cdot COOEt$ , melts at  $90^{\circ}$ . The *acid* forms a white, crystalline powder and melts at  $183-184^{\circ}$ . The *sodium* salt,  $C_{14}H_{13}SO_4Na$ , was obtained in crystalline crusts; the *barium* salt,  $(C_{14}H_{13}SO_4)_2Ba$ , in microscopic, slender needles.

*Ethylic  $\beta$ -naphthylsulphonisobutyrate*,  $C_{10}H_7 \cdot SO_2 \cdot CMe_2 \cdot COOEt$ , is obtained in yellowish-green crystals which melt at  $63-64^{\circ}$ . The *acid* forms white, rhombic crystals melting at  $170^{\circ}$ . The *sodium* salt,  $C_{14}H_{13}SO_4Na$ , is obscurely crystalline; the *barium* salt crystallises in slender, white needles.

When the sodium salt of phenylsulphonebutyric acid is heated, it loses carbonic anhydride, and Otto's normal phenylpropylsulphone is produced. A similar reaction occurs when the corresponding tolylsulphone acid is heated.

*$\alpha$ -Naphthylpropylsulphone*,  $C_3H_7 \cdot SO_2 \cdot C_{10}H_7$ , is made by heating the sodium salt of the corresponding carboxylic acid at  $115^{\circ}$ ; it forms elongated prisms, melts at  $67-68^{\circ}$ , and dissolves in alcohol, ether, acetic acid, benzene, or light petroleum, but is insoluble in water.

*$\beta$ -Naphthylpropylsulphone*,  $C_{13}H_{14}SO_2$ , crystallises in white, felted needles melting at  $73^{\circ}$ .

In order to induce a similar decomposition of the corresponding derivatives of isobutyric acid, it is necessary to heat them with free alkali in closed tubes at  $170^{\circ}$ . The sodium salt of phenylsulphonisobutyric acid, when treated in this way, yields *phenylisopropylsulphone*.

*Paratolylisopropylsulphone*,  $CHMe_2 \cdot SO_2 \cdot C_7H_7$ , crystallises in prisms and melts at  $80^{\circ}$ .

*$\alpha$ -Naphthylisopropylsulphone*,  $CHMe_2 \cdot SO_2 \cdot C_{10}H_7$  forms light yellow, prismatic crystals melting at  $52^{\circ}$ .

*$\beta$ -Naphthylisopropylsulphone* forms crystals melting at  $73^{\circ}$ .

Otto has shown that the sulphonated acetic acid is attacked by halogens without separation of the sulphone group, and that an atom of halogen may be introduced into sulphonated propionic acid, but that the products are so unstable that on boiling they break up into carbonic anhydride and a substituted sulphone. The authors have extended these observations with the following results.

When phenylsulphonebutyric acid is warmed on the water-bath with

bromine and water, the colour disappears, and the product, on fractional crystallisation, may be separated into two substances, one neutral and the other acid. The neutral product is *phenylbromopropylsulphone*,  $\text{CH}_2\text{Me}\cdot\text{CHBr}\cdot\text{SO}_2\text{Ph}$ ; this crystallises in white, feathery needles and melts at  $77-78^\circ$ ; the acid substance is *phenylsulphonebromobutyric acid*,  $\text{C}_{10}\text{H}_{11}\text{BrSO}_4$ , which may be obtained free from the neutral product by conducting the treatment with bromine in sealed tubes at  $100^\circ$  in absence of water; it dissolves in alcohol, ether, acetic acid, or benzene, forms a crystalline powder melting at  $114-115^\circ$ , and when boiled with water breaks up into carbonic anhydride and bromopropylsulphone.

*Paratolylsulphonebromobutyric acid*,  $\text{C}_{11}\text{H}_{13}\text{BrSO}_4$ , melts at  $78-79^\circ$ . *Paratolylmonobromopropylsulphone*,  $\text{CHBrEt}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , forms glassy crystals melting at  $93-94^\circ$ .

When  $\alpha$ -naphthylsulphonebutyric acid is heated with bromine at  $100^\circ$ , a *dibromo-acid*,  $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{SO}_4$ , is obtained which melts and decomposes at  $190^\circ$ . It is probable that in this substance the second bromine atom is in the naphthalene nucleus.

A *dibromo- $\beta$ -naphthylsulphonebutyric acid*,  $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{SO}_4$ , is formed when  $\beta$ -naphthylsulphonebutyric acid is heated with bromine; it melts and decomposes at about  $148^\circ$ .

Phenylsulphonisobutyric acid does not yield a definite product when treated with bromine, but the corresponding paratolyl acid yields a *monobromo-acid*, possibly  $\text{CH}_2\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CMe}_2\cdot\text{COOH}$ , which melts at  $103-104^\circ$ .

$\alpha$ -Naphthylsulphonisobutyric acid, on treatment with bromine, yields a *dibromo-acid*, possibly  $\text{C}_{10}\text{H}_5\text{Br}_2\cdot\text{SO}_2\cdot\text{CMe}_2\cdot\text{COOH}$ , which forms bright yellow leaflets and melts at  $187^\circ$ . A *dibromo-acid* is also obtained from the  $\beta$ -naphthyl compound, and forms yellow leaflets melting at  $195^\circ$ . Neither of the foregoing acids is decomposed when the sodium salt is boiled with water.

The ethylic salts of the sulphonated butyric acids may be brominated at the temperature of the water-bath. *Ethyl phenylsulphonebromobutyrate* was obtained in a crystalline form and gave the corresponding acid on hydrolysis. The bromination of ethyl paratolylsulphonebutyrate gave only ethyl bromide and the monobromo-acid already described; similar results were obtained with the other ethylic salts. Ethyl phenylsulphonisobutyrate gave phenylsulphonisobutyric acid only.

The chlorides of sulphonated butyric acids, unlike those of the corresponding acetic acids, are, as a rule, easily prepared by the action of phosphorus pentachloride on the acid at ordinary or slightly elevated temperatures.

*Phenylsulphonebutyric chloride* forms crystals which melt at  $48^\circ$ . *Paratolylsulphonebutyric chloride* was obtained in the form of an oil which, on treatment with alcohol, gave the corresponding ethylic salt.  *$\alpha$ -Naphthylsulphonebutyric chloride* crystallises in slender, aggregated needles which melt at  $81-82^\circ$ .  *$\beta$ -Naphthylsulphonebutyric chloride* crystallises in nodular aggregates of needles and melts at  $77-78^\circ$ .

*Phenylsulphonisobutyric chloride* forms crystals melting at  $37^\circ$ . *Paratolylsulphonisobutyric chloride* melts at  $38-42^\circ$ .  *$\alpha$ -Naphthyl-*

*sulphonisobutyric chloride* separates from light petroleum in small, rhombic tablets and melts at 75—76°.  $\beta$ -*Naphthylsulphonisobutyric chloride* crystallises in nodular aggregates of needles and melts at 76°.

A. L.

**Reduction of Benzil.** By JOHANNES THIELE (*Annalen*, 1899, 306, 142—145).—The formation of *stilbenediol*,  $\text{OH}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH}$ , as an intermediate product in the reduction of benzil to benzoin, is established by conducting the experiment in presence of concentrated sulphuric acid and acetic anhydride, when the latter arrests the dihydroxy-compound in the form of acetyl derivatives.

The  $\alpha$ -*diacetyl* derivative of stilbenediol crystallises from benzene in small, white needles and melts at 153°; it dissolves less readily in common solvents than the  $\beta$ -*acetyl* derivative, which melts at 110°. Both modifications decolorise an alkaline solution of potassium permanganate, but do not combine readily with ammonia; alcoholic potash converts them into benzoin.

M. O. F.

**Dibenzylidenepropionic Acid and Phenacylcinnamic Acid.** By JOHANNES THIELE (*Annalen*, 1899, 306, 145—171).—*Dibenzylidenepropionic acid*,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{:CHPh})\cdot\text{COOH}$ , prepared by heating dried sodium phenylisocrotonate with acetic anhydride and benzaldehyde at 140° during 20—25 minutes, crystallises from alcohol in pale yellow needles and melts at 167°, diphenylbutadiene (compare Rebuffat, *Abstr.*, 1885, 1137), arising from elimination of carbonic anhydride, being also produced. The *barium*, *calcium*, and *silver* salts are anhydrous; the *methylic* salt is a viscous, brownish-yellow oil. *Meta-nitrodibenzylidenepropionic acid*,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{COOH})\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , obtained from sodium phenylisocrotonate, acetic anhydride, and meta-nitrobenzaldehyde, crystallises from benzene in greenish-yellow plates and melts at 156.5°.

$\alpha$ -*Phenylldihydro- $\beta$ -naphthoic acid*,  $\text{C}_6\text{H}_4\left\langle\begin{array}{l} \text{CH}=\text{C}\cdot\text{COOH} \\ \text{CHPh}\cdot\text{CH}_2 \end{array}\right.$ , or  $\text{C}_6\text{H}_4\left\langle\begin{array}{l} \text{CHPh}\cdot\text{CH}\cdot\text{COOH} \\ \text{CH}=\text{CH} \end{array}\right.$ , produced by molecular rearrangement of

dibenzylidenepropionic acid under the influence of glacial acetic and concentrated sulphuric acids, separates from benzene in a crystalline powder melting at 191°; oxidation with alkaline potassium permanganate converts it into orthobenzoylbenzoic acid.

**3 : 1-Phenylbenzylidenecrotonolactone**,  $\text{CPh}\left\langle\begin{array}{l} \text{CH}\cdot\text{C}\cdot\text{CHPh} \\ \text{O}-\text{CO} \end{array}\right.$ , obtained by adding bromine (1 mol.) to a solution of dibenzylidenepropionic acid in chloroform and then evaporating the solvent, crystallises in golden-yellow leaflets and melts at 150°; concentrated sulphuric acid dissolves it unchanged, developing an intense, reddish-yellow coloration.

*Phenacylcinnamic acid*,  $\text{COPh}\cdot\text{CH}_2\cdot\text{C}(\text{:CHPh})\cdot\text{COOH}$ , prepared by hydrolysing the foregoing lactone, crystallises from alcohol in small prisms and melts at 171°; it forms colourless solutions with alkali carbonates, and becomes intensely yellow with caustic alkalis, yielding salts of the hydroxylic modification,  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{C}(\text{:CHPh})\cdot\text{COOH}$ . Re-

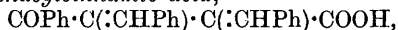
generation of the lactone is brought about by concentrated sulphuric acid and by hot acetic anhydride. The *barium* and *silver* salts are anhydrous; the *methylic* salt crystallises in small prisms melting at 79·5—80°, and yields the *semicarbazone* in colourless needles melting at 179°. *Phenylbenzylidenepyridazone*,  $N \begin{smallmatrix} \text{CPh} \cdot \text{CH}_2 \\ \text{NH} - \text{CO} \end{smallmatrix} > \text{C} : \text{CHPh}$ , pro-

duced on heating an alcoholic solution of methylic phenacylcinnamate with hydrazine hydrate, crystallises from absolute alcohol in white needles and melts at 177°; it is also formed when an alcoholic solution of the semicarbazone is boiled with a small quantity of ammonia. In addition to the phenacylcinnamic acid already described, an *isomeride* is produced when phenylbenzylidenecrotonolactone is hydrolysed, and crystallises from a mixture of benzene and petroleum in small, white needles melting at 127°; acetic anhydride containing a trace of concentrated sulphuric acid converts it into an *isomeride* of phenylbenzylidenecrotonolactone, crystallising from absolute alcohol in long, greenish-yellow needles which melt at 163°.

3 : 1-*Phenylbenzylidenebutylolactone*,  $\text{CHPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{C} : \text{CHPh} \\ \text{O} - \text{CO} \end{smallmatrix}$ , obtained

by reducing a solution of sodium phenacylcinnamate with the copper-zinc couple, crystallises from ether in small needles and melts at 126°; it is insoluble in water, and dissolves with difficulty in organic media.

*Benzylidenephenacylcinnamic acid*,



produced from phenacylcinnamic acid and benzaldehyde under the influence of caustic potash dissolved in methylic alcohol, separates from benzene in a crystalline powder and melts at 171°; concentrated sulphuric acid develops a dark red coloration which quickly becomes bright orange. The *silver* salt is unstable in the dry state.

*Phenacylmethylcinnamic acid*,  $\text{COPh} \cdot \text{CHMe} \cdot \text{C} : (\text{CHPh}) \cdot \text{COOH}$ , prepared by the action of sodium ethoxide on methylic phenacylcinnamate and methylic iodide, followed by hydrolysis of the product, crystallises from benzene in microscopic needles, and melts, evolving gas, at 183—185°; the *sodium* salt contains  $2\frac{1}{2}\text{H}_2\text{O}$ , and the *methylic* salt melts at 90—91°.

*Phenylbenzylidenemethylcrotonolactone*,  $\text{CPh} \begin{smallmatrix} \text{CMe} \cdot \text{C} : \text{CHPh} \\ \text{O} - \text{CO} \end{smallmatrix}$ , pro-

duced by the action of concentrated sulphuric acid on phenacylmethylcinnamic acid dissolved in acetic anhydride, crystallises from alcohol in long, yellow, highly refractive needles and melts at 128—128·5°; boiling sodium carbonate regenerates phenylmethylcinnamic acid.

M. O. F.

**Phenacylbromocinnamic Acid.** By JOHANNES THIELE and ERNST MAYR (*Annalen*, 1899, 306, 171—175).—*Phenylbromobenzylidenecrotonolactone*,  $\text{C}_{17}\text{H}_{11}\text{BrO}_2$ , prepared by adding bromine to phenylbenzylidenecrotonolactone dissolved in chloroform, crystallises from alcohol in yellow needles and melts at 128·5°.

*Phenacylbromocinnamic acid*,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{C} : (\text{CPhBr}) \cdot \text{COOH}$ , produced when bromine acts on phenylbenzylidenecrotonolactone or on

phenacylcinnamic acid in glacial acetic acid, crystallises from benzene in nodules; it melts and evolves gas at  $137^{\circ}$ , becoming solid immediately afterwards, and subsequently fusing at about  $200^{\circ}$ . Phenacylcinnamic acid is regenerated on reduction with zinc dust and glacial acetic acid.

Diphenylfurfurancarboxylic acid, described by Paal and Kapf, occurs as a bye-product in preparing the foregoing bromo-derivatives; it is also obtained on keeping a solution of phenacylbromocinnamic acid in caustic alkali at ordinary temperatures during 24 hours. The *methylic* salt melts at  $63^{\circ}$ . M. O. F.

**Phenacylhydrocinnamic Acid and the Dibromide of Dibenzylidenepropionic Acid.** By JOHANNES THIELE and ERNST MAYR (*Annalen*, 1899, 306, 176—193).—The *dibromide of dibenzylidenepropionic acid*,  $\text{CHPhBr} \cdot \text{CH} : \text{C}(\text{CHPhBr}) \cdot \text{COOH}$ , occurs in the mother liquor when 3:1-phenylbenzylidenecrotonolactone is recrystallised from alcohol, and is separated from the lactone by its insolubility in water; benzene deposits it in the form of a snow-white, crystalline powder which melts at about  $194^{\circ}$ , when it becomes red and evolves gas. Reduction with zinc dust and glacial acetic acid converts it into dibenzylidenepropionic acid.

*Phenylbromobenzyl- $\alpha$ -crotonolactone*,  $\text{CHPh} \cdot \text{CH} \begin{array}{c} \diagup \\ \text{O} \text{---} \text{CO} \end{array} \text{C} \cdot \text{CHPhBr}$ , obtained by the action of aqueous sodium carbonate on the dibromide of dibenzylidenepropionic acid dissolved in alcohol, becomes deep yellow at about  $120^{\circ}$ , and melts, evolving gas, at  $130^{\circ}$ ; hydrogen bromide is eliminated very readily, phenylbenzylidenecrotonolactone being formed.

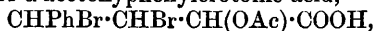
*Phenacylhydrocinnamic acid*,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_2\text{Ph}) \cdot \text{COOH}$ , produced from phenylbenzylidenecrotonolactone, by reduction with zinc dust and glacial acetic acid, is also formed on reducing phenacylcinnamic acid; it crystallises from methylic alcohol in white needles and melts at  $169.5^{\circ}$ . The *methylic* salt melts at  $68.5^{\circ}$ , and yields the *phenylhydrazone* in white needles which melt and decompose at  $106^{\circ}$ .

3:1-*Phenylbenzyl- $\beta$ -crotonolactone*,  $\text{CHPh} \cdot \text{CH} \begin{array}{c} \diagup \\ \text{O} \text{---} \text{CO} \end{array} \text{CH} \cdot \text{CH}_2\text{Ph}$ , the labile lactone of phenacylhydrocinnamic acid, prepared by cautiously reducing phenylbenzylidenecrotonolactone with alcoholic sulphuric acid and zinc dust, is also formed when a few drops of concentrated sulphuric acid are added to a solution of phenacylhydrocinnamic acid in acetic anhydride; it crystallises from methylic alcohol in white needles, and melts at  $100\text{--}101^{\circ}$ . The lactone reduces alkaline potassium permanganate and ammoniacal silver solutions, and bromine dissolved in carbon bisulphide gives rise to hydrogen bromide; glacial acetic acid which has been saturated with hydrogen bromide resolves it into phenacylhydrocinnamic acid.

3:1-*Phenylbenzyl- $\alpha$ -crotonolactone*,  $\text{CHPh} \cdot \text{CH} \begin{array}{c} \diagup \\ \text{O} \text{---} \text{CO} \end{array} \text{C} \cdot \text{CH}_2\text{Ph}$ , the stable lactone of phenacylhydrocinnamic acid, arises from the labile modifi-

cation under the influence of boiling acetic anhydride, and is also obtained by reducing the lactone of phenacylbromohydrocinnamic acid with zinc dust and glacial acetic acid; it crystallises from light petroleum in colourless leaflets, and melts at 67°. The stable lactone decolorises alkaline potassium permanganate, but does not unite with bromine; it is stable towards boiling dilute hydrochloric acid, which resolves the labile modification into phenacylhydrocinnamic acid, but undergoes hydrolysis when treated with a solution of hydrogen bromide in glacial acetic acid.

The *dibromide* of  $\alpha$ -acetoxyphenylcrotonic acid,



prepared by the action of hydrogen bromide in glacial acetic acid on the dibromide of phenylhydroxyerotic acid, forms a white, crystalline powder; which becomes reddish at about 180°, and melts, evolving gas, at 207°.

M. O. F.

**Isomeric Diphenylcrotonolactones.** By JOHANNES THIELE (*Annalen*, 1899, 306, 194—197).—Diphenylcrotonolactone, first obtained by Klingemann, and subsequently by Erlenmeyer and Lux (*Abstr.*, 1898, i, 668), has been hitherto regarded as the  $\beta\gamma$ -unsaturated lactone; as it has become possible to prepare a labile modification (compare foregoing abstract), the author regards this substance as having the constitution in question, the stable isomeride being unsaturated in the  $\alpha\beta$ -position.

Labile *diphenylcrotonolactone*,  $\begin{array}{c} \text{CPh}:\text{CPh} \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{O}$ , prepared by adding a few drops of concentrated sulphuric acid to desylacetic acid suspended in acetic anhydride, crystallises from a mixture of light petroleum and benzene in small, white needles, and melts at 99.5—100.5°; alcoholic potash regenerates desylacetic acid. The stable lactone,  $\begin{array}{c} \text{CPh} \cdot \text{CHPh} \\ | \\ \text{CH}-\text{CO} \end{array} > \text{O}$ , obtained on treating the labile modification with boiling acetic anhydride, is identical with the compound described by Klingemann (*Abstr.*, 1892, 1002).

M. O. F.

**Preparation of Phenylcinnamenylacrylic Acid and of Diphenylbutadiene.** By JOHANNES THIELE and KARL SCHLEUSSNER (*Annalen*, 1899, 306, 197—201).—The authors describe improvements in Rebuffat's methods of preparing phenylcinnamenylacrylic acid, diphenylbutadiene (diphenyldiethylene), and its dibromide (compare *Abstr.*, 1885, 1137, and 1891, 76).

M. O. F.

**The Dibromide of Phenylcinnamenylacrylic Acid.** By JOHANNES THIELE and HEINRICH RÖSSNER (*Annalen*, 1899, 306, 201—224).—2 : 5-Diphenyl-2 : 5-dibromo-3-pentenoic acid, the *dibromide* of phenylcinnamenylacrylic acid,  $\text{CHPhBr} \cdot \text{CH} : \text{CH} \cdot \text{CPhBr} \cdot \text{COOH}$ , prepared by the action of bromine (1 mol.) on phenylcinnamenylacrylic acid dissolved in carbon bisulphide, crystallises from a mixture of benzene and light petroleum, and melts at 174—175°, when it decomposes; the *methylic* salt melts at 117—118°.

*Diphenyldihydrofurfuran*,  $\begin{array}{c} \text{CH} \cdot \text{CHPh} \\ | \\ \text{CH} \cdot \text{CHPh} \end{array} > \text{O}$ , is formed from the dibromide

of phenylcinnamenylacrylic acid under the influence of sodium carbonate, sodium acetate, or caustic alkalis; it melts at 88—89°, and exhibits the behaviour of an unsaturated compound. Tetrabromodiphenylfurfuran,  $\begin{array}{c} \text{CBr}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \\ | \\ \text{CBr}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{array} > \text{O}$ , obtained by exposing the finely powdered furfuran derivative to the action of bromine vapour during 24 hours, is identical with the compound,  $\text{C}_{10}\text{H}_{10}\text{Br}_4\text{O}$ , described by Perkin (Trans., 1890, 57, 954); oxidation with chromic acid dissolved in glacial acetic acid converts it into parabromobenzoic acid. *Pentabromodiphenylfurfuran*,  $\begin{array}{c} \text{CBr}:\text{C}(\text{C}_6\text{H}_3\text{Br}_2) \\ | \\ \text{CBr}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{array} > \text{O}$ , produced when diphenylfurfuran is exposed to bromine vapour during 48 hours, crystallises from benzene in white needles and melts at 209—210°.

*Tribromodiphenylfurfuran*,  $\begin{array}{c} \text{CBr}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \\ | \\ \text{CH}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{array} > \text{O}$ , prepared by reducing tetrabromodiphenylfurfuran with zinc dust and glacial acetic acid, crystallises from alcohol in slender, white needles and melts at 134°. The product of further reduction is *paradibromodiphenylfurfuran*,  $\begin{array}{c} \text{CH}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \\ | \\ \text{CH}:\text{C}(\text{C}_6\text{H}_4\text{Br}) \end{array} > \text{O}$ , which crystallises from benzene in aggregates of long, slender needles, and melts at 201°; oxidation converts it into parabromobenzoic acid. The *dibromide* of diphenyldihydrofurfuran,  $\begin{array}{c} \text{CHBr}:\text{CHPh} \\ | \\ \text{CHBr}:\text{CHPh} \end{array} > \text{O}$ , obtained on adding bromine (1 mol.) to a solution of diphenyldihydrofurfuran in carbon bisulphide, crystallises from alcohol in groups of small needles and melts at 110—111°.

*Phenylbromocinnamenylacrylic acid*,  $\text{CPhBr}:\text{CH}:\text{CH}:\text{CPh}:\text{COOH}$ , a bye-product in the preparation of diphenyldihydrofurfuran from the dibromide of phenylcinnamenylacrylic acid, crystallises from methylic alcohol in nodules, and melts at 213—214°, evolving gas; the *potassium* and *sodium* salts contain  $2\frac{1}{2}\text{H}_2\text{O}$ , and the *methylic* salt melts at 127—128°.

*Diphenylbutenincarboxylic acid*,  $\text{CPh}:\text{C}:\text{CH}:\text{CPh}:\text{COOH}$ , prepared by heating phenylbromocinnamenylacrylic acid with alcoholic sodium methoxide during 20—30 hours at 170—180°, crystallises from benzene in slender, white needles; reduction with sodium amalgam in glacial acetic acid and alcohol converts it into 2:5-diphenyl-3-pentenoic acid (following abstract), which melts at 101—102°.

Cornicularolactone,  $\begin{array}{c} \text{CPh}:\text{CH}:\text{C}:\text{CHPh} \\ | \quad \quad | \\ \text{CO} \quad \quad \text{O} \end{array}$ , produced by the action of diethylaniline on the dibromide of phenylcinnamenylacrylic acid at 150°, melts at 141—142°, and is identical with the compound described by Spiegel (Abstr., 1882, 1077). Cornicularic acid,  $\text{CH}_2\text{Ph}:\text{CO}:\text{CH}:\text{CHPh}:\text{COOH}$ , prepared from the lactone by hydrolysis, crystallises from benzene in colourless plates, and melts at 122—123°; the *sodium* salt contains  $2\frac{1}{2}\text{H}_2\text{O}$ , and the *methylic* salt, which crystallises in white leaflets, melts at 95°.

*Phenylbenzylpyridazone*,  $\text{N} \begin{array}{c} \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH} \\ \text{NH} \quad \quad \text{CO} \end{array} > \text{CPh}$ , formed when

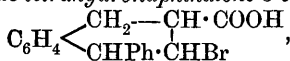
methylic cornicularate is heated with semicarbazide in glacial acetic acid, crystallises from alcohol in lustrous, white needles, and melts at  $215^{\circ}$ .

*Methylic benzylidenecornicularate*,  $\text{CHPh}:\text{CPh}:\text{CO}:\text{CH}:\text{CPh}:\text{COOMe}$ , obtained from methylic cornicularate and benzaldehyde under the influence of pyridine, crystallises from alcohol in long, yellow needles, and melts at  $138-139^{\circ}$ .

*Diphenyldianilidobutene*,  $\text{C}_6\text{H}_4\text{Ph}_2(\text{NHPh})_2$ , prepared by digesting diphenylbutadiene dibromide with aniline at  $40-45^{\circ}$ , crystallises from alcohol, and melts at  $138-139^{\circ}$ . M. O. F.

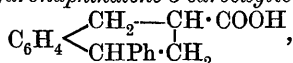
**Reduction of Dibenzylidenepropionic Acid and of Phenylcinnamylacrylic Acid.** By JOHANNES THIELE and JAKOB MEISENHEIMER (*Annalen*, 1899, **306**, 225-240).— *$\alpha$ -Phenylbenzylisocrotonic acid*,  $\text{CH}_2\text{Ph}:\text{CH}(\text{COOH})\cdot\text{CH}:\text{CHPh}$ , prepared by reducing an alcoholic solution of dibenzylidenepropionic acid with glacial acetic acid and sodium amalgam, crystallises from 85 per cent. alcohol in colourless prisms and melts at  $124^{\circ}$ .

*2:1-Bromophenyl-ac-tetrahydronaphthalene-3-carboxylic acid*,



produced on adding bromine (1 mol.) to an ice-cold solution of phenylbenzylisocrotonic acid in chloroform, crystallises from methylic alcohol in white needles and melts at  $204-205^{\circ}$ ; the solution in sodium carbonate does not decolorise potassium permanganate.

*1-Phenyl-ac-tetrahydronaphthalene-3-carboxylic acid*,

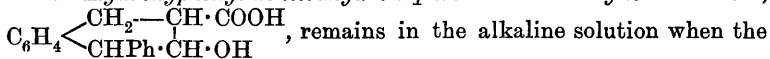


prepared by reducing the foregoing substance with glacial acetic acid and zinc dust, is also formed when benzylphenylisocrotonic acid is treated with a boiling mixture of glacial acetic and sulphuric acids during 7 hours; it crystallises from methylic alcohol in lustrous needles melting at  $177^{\circ}$ , and does not decolorise potassium permanganate. The sodium salt contains  $6\text{H}_2\text{O}$ , and the methylic salt melts at  $82^{\circ}$ ; oxidation converts the acid into orthobenzoylbenzoic acid.

*1:4-Dihydro-1-phenylnaphthalene*,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CH}_2-\text{CH} \\ \text{CHPh}\cdot\text{CH} \end{array}$ , obtained from

bromophenyltetrahydronaphthalenecarboxylic acid by the action of a boiling solution of sodium carbonate in slight excess, crystallises from methylic alcohol in lustrous needles and melts at  $50^{\circ}$ ; its behaviour towards solutions of potassium permanganate and bromine is that of an unsaturated compound.

*2:1-Hydroxyphenyl-ac-tetrahydronaphthalene-3-carboxylic acid*,



foregoing hydrocarbon has been removed with ether; it crystallises from benzene in cubes and melts at  $194^{\circ}$ .

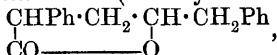
*2:5-Diphenyl-3-pentenoic acid*,  $\text{CH}_2\text{Ph}:\text{CH}:\text{CH}:\text{CHPh}:\text{COOH}$ , prepared by reducing an alcoholic solution of  $\alpha$ -phenylcinnamylacrylic acid with glacial acetic acid and sodium amalgam, crystallises from alcohol in plates and melts at  $101.5^{\circ}$ ; it decolorises a solution of potassium



permanganate instantly. The *sodium* salt is readily soluble in water, and the *calcium* salt crystallises in slender, silky needles containing  $2\text{H}_2\text{O}$ , which is removed at  $105^\circ$ .

2:5-Diphenyl-2-pentenoic acid,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOH}$ , obtained on heating the foregoing acid with 10 per cent. caustic soda during 20 hours on the water-bath, crystallises from light petroleum in lustrous, silky needles melting at  $88^\circ$ ; it instantly decolorises an alkaline solution of potassium permanganate. The *sodium* salt contains  $5\text{H}_2\text{O}$ , and crystallises in lustrous needles; it is less readily soluble than the sodium salt of the isomeride.

2:5-Diphenyl-1:4-pentanolid (tetrahydrocornicularolactone),



obtained from 2:5-diphenyl-3-pentenoic acid by the action of glacial acetic and concentrated sulphuric acids, is identical with the compound described by Spiegel (Abstr., 1882, 1077); the *silver* salt of the corresponding hydroxy-acid is amorphous. M. O. F.

**Unsymmetrical Tetramethyldiamidodiphenylethane.** By AUGUST TRILLAT (*Compt. rend.*, 1899, 128, 1113—1115).—The *unsymmetrical tetramethyldiamidodiphenylethane*,  $\text{CHMe}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , crystallises in colourless lamellæ melting at  $68\text{--}69^\circ$ ; it is insoluble in water but readily dissolves in the ordinary organic solvents and also dilute acids, with which it forms well crystallised salts. It is prepared by mixing the volatile product of the oxidation of ethylic alcohol by chromic acid mixture with dimethylaniline and 20 per cent. sulphuric acid and warming the mixture for several days. The excess of aldehyde is distilled off, the mixture rendered alkaline and distilled with steam, and the residue crystallised from light petroleum and alcohol. The yield is 70 per cent. of the dimethylaniline employed. The *platinochloride* is slightly soluble in water and dilute hydrochloric acid, and crystallises in orange prisms decomposing at  $210\text{--}211^\circ$ . When the substance is oxidised with lead peroxide in acetic acid solution, a deep greenish-blue coloration is developed which disappears on warming the solution. G. T. M.

NOTE.—Two other isomerides of this base are already known, the symmetrical compound,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , melting at  $50^\circ$  (Abstr., 1879, 714, and 1887, 673), and the substance, melting at  $87^\circ$ , obtained by the action of zinc and hydrochloric acid on a mixture of dimethylaniline and carbon bisulphide (Tröger, Abstr., 1888, 286). G. T. M.

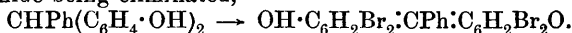
1:1-Diphenylbutene-1-one (3). By AUGUST KLAGES and E. FANTO (*Ber.*, 1899, 32, 1433—1436).—*Ethylic  $\alpha$ -acetyl- $\beta\beta$ -diphenyl acrylate*,  $\text{CMeO}\cdot\text{C}(\text{COOEt})\cdot\text{CPh}_2$ , is best prepared by boiling benzophenone chloride in benzene solution for several hours with ethylic cupracetoacetate (obtained by mixing alcoholic ethylic acetoacetate with an ammoniacal aqueous solution of copper acetate at  $0^\circ$ ), diluting with ether, filtering from cuprous chloride, shaking the solution repeatedly with water and then with dilute alkali, evaporating it, and cooling the residual oil with ice. It melts at  $76^\circ$ , forms an *oxime*

melting at 136—138°; with phenylhydrazine, it yields a yellow *pyrazolone* derivative,  $\begin{matrix} \text{N}=\text{CMe} \\ \text{NPh} \cdot \text{CO} \end{matrix} > \text{C}:\text{CPh}_2$ , melting at 182—183°; it shows no disposition to form additive products with ethylic acetoacetate, benzylic cyanide, or deoxybenzoin, and yields the *acid*  $\text{CMeO} \cdot \text{C}(\text{COOH}):\text{CPh}_2$  when boiled with alcoholic potash. This acid melts at 143°, and its unstable *silver* salt at 169—170°; when the acid is distilled under diminished pressure, it yields 1:1-*diphenylbutene-1-one-3*,  $\text{CMeO} \cdot \text{CH}:\text{CPh}_2$ , which boils at 190° under 13 mm. pressure, melts at 33°, has a sp. gr. 1.080 at 16°/4°, and forms an *oxime* melting at 88°. C. F. B.

**Hydrocinnamoin.** By JOHANNES THIELE (*Ber.*, 1899, 32, 1296—1297).—Cinnamaldehyde, when reduced with the zinc-copper couple in alcoholic solution, yields large quantities of *hydrocinnamoin*,  $\text{C}_2\text{H}_5(\text{OH})_2(\text{CH}:\text{CHPh})_2$ , a white, crystalline substance separating from alcohol in leaflets melting at 153—154°. The *diacetate*, which melts at 118—119°, forms small, white prisms, and the *dibenzoate* slender, colourless needles melting at 169—170°.

When the thick oil, which is the chief product in this reduction, is distilled, it yields a brown distillate, from which, after a time, white leaflets of a hydrocarbon of the formula  $\text{C}_{18}\text{H}_{14}$  separate; this melts at 205—207°, and is sparingly soluble in alcohol; it is probable that it is phenyl-*a*-naphthylethylene. J. F. T.

**Methylenequinones of the Dibenzyl and Stilbene Series, and the Corresponding Ketochlorides.** By THEODOR ZINCKE (*J. pr. Chem.*, 1899, [ii], 59, 228—244.—In analogy with previous work (this vol., i, 265), dihydroxytriphenylmethane, on bromination, yields tetrabromohydroxydiphenylmethylenequinone, 1 mol. of hydrogen bromide being eliminated,



The reaction holds also for the stilbene and dibenzyl series.

Paradiamidotolane, when acted on by chlorine, yields the ketochloride,  $\text{C}_6\text{H}_4\text{Cl}_2\text{O} \cdot \text{CCl}:\text{CCl} \cdot \text{C}_6\text{H}_4\text{Cl}_2\text{O}$ , in two forms, melting at 246—247° and 212° respectively; each, on reduction, gives the same dihydric phenol,  $\text{C}_{14}\text{H}_6\text{Cl}_6\text{O}_2$ , melting at 248°. By the further action of chlorine, the phenol yields a white additive product melting at 222° and a red compound melting at 248°, the latter being converted into the former by the action of hydrogen chloride in acetic acid solution, whilst the white product, when heated with alcohol or aqueous acetone, loses hydrogen chloride and passes into the red compound, thus,



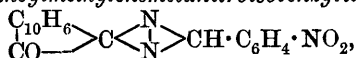
The *diacetyl* derivative of the white compound forms thick, colourless crystals and melts at 176—177°. When heated with water, alcohol, or acetic acid, the red compound is converted into a colourless phenolic derivative,  $\text{OH} \cdot \text{C}_6\text{H}_4\text{Cl}_2 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl}_2 \cdot \text{OH}$ , which melts at 275°, and yields an azine when treated with orthophenylenediamine. When the phenol,  $\text{C}_{14}\text{H}_6\text{Cl}_6\text{O}_2$ , is treated with bleaching powder, it is converted into the compound  $\text{C}_2\text{Cl}_2(\text{C}_6\text{H}_4\text{Cl}_3\text{O})_2$ , which melts at 185°.

Paradihydroxystilbene, when treated with excess of chlorine, yields a hexachloro-derivative,  $\text{C}_2\text{H}_2\text{Cl}_2(\text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{OH})_2$ , which, however, at

once passes into the more stable ketonic form,  $C_2H_2Cl_2(C_6H_3Cl_2\cdot O)_2$ ; this forms colourless needles, and decomposes when heated; when warmed with alcohol or acetone and water, it loses 2 mols. of hydrogen chloride and passes into the quinone,  $C_2H_2(C_6H_2Cl_2\cdot O)_2$ , which resembles amorphous phosphorus in appearance. Treatment with stannous chloride reduces the quinone to tetrachlorodihydroxystilbene, whilst hydrogen chloride reconverts it into the hexachloride. When heated in sealed tubes with methylic or ethylic alcohol, the quinone is converted into colourless compounds of the formula  $C_2H_2(OR)_2(C_6H_2Cl_2\cdot OH)_2$  where  $R = Me$  or  $Et$ .  
F. H. N.

**Action of Isobutylic Bromide on  $\beta$ -Naphthyllic Methylic Ether in Presence of Anhydrous Aluminium Chloride.** By E. CAHEN (*Bull. Soc. Chim.*, 1898, [iii], 19, 1007—1008).—When isobutylic bromide is gradually added to a solution of  $\beta$ -naphthyllic methylic ether and aluminium chloride in carbon bisulphide, the liquid heated at  $65^\circ$  for 3 hours, and the product fractionally distilled, a substance,  $OMe\cdot C_{10}H_6\cdot CH_2\cdot CHMe_2$ , is obtained which crystallises from alcohol in slender, prismatic needles melting at  $66^\circ$  and boiling at about  $188^\circ$  under 14 mm. pressure; it is decomposed with difficulty by boiling alkalis.  
N. L.

**Condensation of Acenaphthenequinone and Hydrazine Hydrate.** By JOACHIM HERMS (*Chem. Centr.*, 1899, i, 114—115; from *Diss. Kiel.*, 1898).—*Perinaphthoylhydrazimethylene*,  $\begin{matrix} C_{10}H_6 \\ CO- \end{matrix} > C < \begin{matrix} NH \\ NH \end{matrix}$  prepared by slowly adding hydrazine hydrate to acenaphthaquinone suspended in boiling alcohol, separates in small crystals, is easily soluble in hot alcohol, ether, benzene, or chloroform, slightly in hot water, and with concentrated sulphuric acid gives a characteristic violet coloration. Whilst by the action of benzaldehyde on this compound, only tarry products are obtained, with metanitrobenzaldehyde it forms *perinaphthoylmethylenemetanitroisobenzylideneazine*,



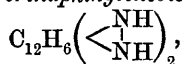
which crystallises in small, yellow needles, melts and decomposes at  $253^\circ$ , and is easily soluble in hot nitrobenzene, almost insoluble in alcohol or ether. *Perinaphthoylhydrazimethylene* is not oxidised as readily as Curtius's benzoylphenylhydrazimethylene, but when dissolved in benzene and treated with mercuric oxide, it yields *perinaphthoylazo-*

*methylene*,  $C_{12}H_6O < \begin{matrix} N \\ N \end{matrix}$ , which separates from light petroleum in small crystals, melts at  $79-80^\circ$ , and is easily soluble in ether, alcohol, or chloroform, and insoluble in water; from the mother liquor, crystals melting at  $94-102^\circ$  were obtained. By the action of bromine on the

azo-compound, *perinaphthoyldibromomethylene*,  $C_{10}H_6 < \begin{matrix} CBr_2 \\ CO \end{matrix}$ , melting at  $160-161^\circ$ , is formed.

*Perinaphthylenehydrazimethylenemetanitroisobenzylideneazine*, possibly of the composition,  $\begin{matrix} NH \\ NH \end{matrix} > C < \begin{matrix} C_{10}H_6 \\ \end{matrix} > C < \begin{matrix} N \\ N \end{matrix} > CH\cdot C_6H_4\cdot NO_2$ , obtained

by heating the nitroisobenzylideneazine with hydrazine hydrate for 6 hours at  $110^{\circ}$ , crystallises in yellow plates and melts at  $215\text{--}216^{\circ}$  with liberation of nitrogen. *Perinaphthylenebis-hydrazimethylene*,



prepared by heating perinaphthoylhydrazine hydrate with alcohol on the water-bath, crystallises in pale yellow needles, melts at  $192^{\circ}$ , and is easily soluble in hot alcohol and hot chloroform, and insoluble in cold water. *Perinaphthylenebismetanitroisobenzylideneazine*,

$\text{C}_{12}\text{H}_6\left(\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array}\right)\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , is obtained by heating a mixture of the dihydrazimethylene with metanitrobenzaldehyde on the water-bath; it crystallises in lustrous plates and prisms, melts at  $246^{\circ}$ , and is easily soluble in hot nitrobenzene and almost insoluble in alcohol or ether. Attempts to prepare perinaphthoylmonochloromethylene yielded a substance which melted at  $109\text{--}110^{\circ}$ . A comparison with the corresponding benzil and acenaphthenequinone derivatives shows that as the melting points rise in the one series they sink in the other, and *vice versa*.  
E. W. W.

**Structure of Terpenes and Allied Compounds.** The Terpene from Solid Pinene Dibromide. By GODLEWSKI and GEORG WAGNER (*Chem. Centr.*, 1897, i, 1055; from *J. Russ. Chem. Soc.*, 1896, 29, 121).—When Wallach's pinene dibromide (m. p.  $169\text{--}170^{\circ}$ ) is treated with zinc dust and acid, the terpene  $\text{C}_{10}\text{H}_{16}$  is produced; it melts at  $65\text{--}66^{\circ}$ , and boils at  $153^{\circ}$ . The hydrocarbon is indifferent towards potassium permanganate, but yields a solid additive compound with hydrogen chloride. If the new terpene does not contain an ethylenic linking, it represents a new type of hydrocarbon, to which the authors give the name *tricyclene*; such a substance would be the analogue of anthracene and phenanthrene.  
M. O. F.

**Action of Hypochlorous Acid on Pinene.** By ALEXANDER GINZBERG and E. WAGNER (*Chem. Centr.*, 1899, i, 50; from *J. Russ. Chem. Soc.*, 1898, 30, 675—680).—By the action of hypochlorous acid on French turpentine of specific rotatory power  $[\alpha]_D - 37^{\circ} 50'$ , and melting at  $155.5\text{--}156.5^{\circ}$ , a *chlorhydrin* is obtained which melts at  $131\text{--}132^{\circ}$  and has a specific rotatory power  $[\alpha]_D + 88^{\circ} 23'$ . This compound, when mixed with an equal weight of the *laevochlorhydrin* of the same melting point prepared from dextropinene, forms the inactive chlorhydrin which is also obtained from dextropinene, and melts at  $104\text{--}105^{\circ}$ . By adding hypochlorous acid to an emulsion of pinene in water, treating the product with potassium carbonate, extracting with ether (compare preceding abstract), and distilling in steam, tricyclene dichloride,  $\text{C}_{10}\text{H}_{16}\text{Cl}_2$ , is obtained; it separates in monoclinic crystals (Wulff) and melts at  $165\text{--}168^{\circ}$ .  
E. W. W.

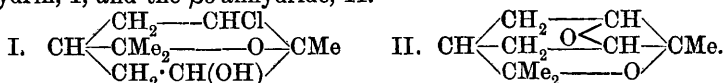
**Pinol Chlorhydrin.** By ALEXANDER GINZBERG (*Chem. Centr.*, 1899, i, 50; from *J. Russ. Chem. Soc.*, 1898, 30, 681—685).—By the action of hypochlorous acid on pinol, a *chlorhydrin* is obtained which crystallises from light petroleum in long needles, melts at  $52\text{--}54^{\circ}$ , is easily

soluble in alcohol, ether, chloroform, benzene, or ethylic acetate, and is more soluble in water than the pinene chlorhydrin; the aqueous solution rapidly becomes acid. By the action of potassium hydroxide at the ordinary temperature, it forms the anhydride of pinolglycol obtained by Wallach from sobrerol dibromide, and pinene glycol is formed by treating the anhydride with dilute sulphuric acid (1:50), or by heating it with water on the water-bath for 7 hours, or from the chlorhydrin itself by boiling with water for 10 hours. Since the chlorhydrin, when oxidised with chromic acid at 0°, gives a product which, with phenylhydrazine acetate, forms a hydrazone, its composition is probably

$$\begin{array}{c} \text{O} - \text{CH} - \text{CMeCl} \\ | \quad \diagup \quad \diagdown \\ \text{CMe}_2 \cdot \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} \cdot \text{OH} \end{array}$$
 The oxidation product crystallises in long needles and melts at 74–75.5°, and the hydrazone melts at 107–108°.

E. W. W.

**Structure of the Chlorhydrins and their Derivatives obtained by the Action of Hypochlorous Acid on Pinene.** By ALEXANDER GINZBERG (*Chem. Centr.*, 1899, i, 50–51; from *J. Russ. Chem. Soc.*, 1898, 30, 686–693).—The syrupy product obtained by the action of hypochlorous acid on pinene is a mixture of several compounds, only one of which, when treated with potassium hydroxide yields the *cis*- and *trans*-stereoisomerides of the crystalline chlorhydrin, I, and the  $\beta\delta$ -anhydride, II.



This anhydride cannot be obtained from the chlorhydrin, and is not identical with the anhydride of pinolglycol prepared from sobrerol dibromide. The structural formulæ of the dichlorhydrins are easily derived from these.

E. W. W.

**Caryophyllene Derivatives.** By EDWARD KREMERS, OSWALD SCHREINER, and CHARLOTTE F. JAMES (*Pharm. Archives*, 1898, 1, 209–215; compare Chapman, *Trans.*, 1895, 54, 780). A comparison of the properties of the derivatives of caryophyllene and humulene shows that these substances are not identical. From caryophyllene of sp. gr. 0.9032 at 20°, specific rotatory power  $[\alpha]_D - 8.74^\circ$ , and specific refractive index  $n_D 1.50019$ , a nitrosochloride which melts at 158–160° was prepared by Wallach's method, using gaseous hydrogen chloride, however, instead of its solution. Caryophyllene *nitrosate* crystallises in slender needles, melts at 147–150°, is insoluble in alcohol and ether, rather soluble in benzene and chloroform, and slightly so in glacial acetic acid; when boiled for a short time with alcoholic potash, it forms a compound which crystallises in white needles, melts at 220–223°, and is probably the oxime. The *nitrosite*, prepared by treating a mixture of equal volumes of caryophyllene and light petroleum with a concentrated aqueous solution of sodium nitrite and glacial acetic acid, crystallises in blue needles, forms a blue solution in alcohol, and melts at 107°; the blue colour may be removed by recrystallising. Caryophyllene isonitrosite (Chapman, *Trans.*, 1895,

782), or bisnitrosite (Baeyer), obtained by heating the alcoholic solution of the nitrosite, crystallises in colourless forms and melts at 53—56°. *Caryophyllene nitrolbenzylamine* and *nitrolpiperidine* separate in white crystals and melt at 125—128° and 141—142° respectively. Humulene nitrosochloride melts at 164—165°, the nitrosate at 162—163°, the nitrosite at 120—121°, the isonitrosite at 165—168°, the nitrolbenzylamine at 136°, and the nitrolpiperidine at 153°.

E. W. W.

**Essential Oils of Neroli and Petit Grain.** By EUGÈNE CHARABOT and L. PILLET (*Bull. Soc. Chim.*, 1898, [iii], 19, 853—857).—In view of sundry discrepancies between the observations of previous experimenters, the authors have themselves distilled and examined nine specimens of oil of neroli and eight of oil of petit grain, a common adulterant of the former. The results obtained may be summarised as follows:

	Oil of neroli.	Oil of petit grain.
Sp. gr. at 15° .....	0.872—0.876	0.891—0.894
Rotation per 100 mm. at 15° .....	+1.42—4.06°	—4.45—6.00°
Index of refraction $n_D$ at 18—21°	1.470—1.4745	—
Ethereal salts calculated as		
$C_{10}H_{17} \cdot OAc$ , per cent. ....	10.1—18.0	51.5—69.6
Parts of 80 per cent. alcohol required for solution at 20° ...	1.3—1.55	1—1.1

One of the specimens of oil of neroli was insoluble in alcohol; the solubility appears to diminish with age. The difference in the rotatory powers of the two oils is shown by fractional distillation to be due to the fact that oil of neroli contains a larger proportion of dextro-rotatory terpene and a smaller proportion of alcohols than does oil of petit grain. The alcohols, linalool and geraniol, contained in the two oils are qualitatively identical, although their relative proportions and the nature of the acids with which they are partially combined are different. It is to the ethereal salts present that the characteristic odours of the oils are due, since after hydrolysis both are found to possess a similar odour, recalling that of linalool.

N. L.

**An Important Constituent of Oil of Neroli.** By HEINRICH WALBAUM (*J. pr. Chem.*, 1899, [ii], 59, 350—352).—By shaking French oil of orange-blossoms with 30 per cent. sulphuric acid, a basic substance was obtained which proved to be the methylic salt of anthranilic acid; it was also isolated from oil prepared by Schimmel and Co. from orange-blossoms which had been preserved in salt.

The substance was obtained as a colourless oil which gradually solidified. The crystals have a blue fluorescence, a property which is also exhibited in a marked degree by the alcoholic solution. The odour of the undiluted substance is not pleasant, but that of dilute solutions recalls that of orange-blossoms. It is easily prepared synthetically by the action of methylic alcohol and hydrogen chloride or sulphuric acid on anthranilic acid, and the synthetical substance has the same properties as the naturally occurring compound. It boils at 132° under a pressure of 14 mm., has a sp. gr. 1.168 at 15°.

melts at 24—25°, and resolidifies at 24° (compare E. von Meyer and G. Schmidt, *Abstr.*, 1888, 371). A. L.

**Oil of Neroli.** By ERNST ERDMANN and HUGO ERDMANN (*Ber.*, 1899, 32, 1213—1219).—Oil of orange-blossoms (*Essence de Néroli pétales*, *Néroli Bigarade*, &c.) contains a small quantity of *methylic anthranilate*, which was isolated and compared with the pure compound. It forms large crystals, melts at 24·5°, boils at 127° under 11 mm. pressure, and has a sp. gr. 1·163 at 26°. The crystals have a blue fluorescence, and the fluorescence of oil of orange-blossoms is no doubt due to the presence of this compound. About 2 grams of the hydrochloride were obtained from 1 kilo. of the oil. The *hydrochloride* melts at 178°, the *benzoyl* derivative at 99—100°.

*Ethylic anthranilate* melts at 13°, and boils at 136—137° under 13·5 mm. pressure. The odour of this compound is much fainter and coarser than that of the methylic salt.

Some specimens of oil of orange-blossoms contain small amounts of pyrroline derivatives, and these are always present in the oil of petit grain of commerce. The compound present is probably a nitrogen alkyl derivative, but has not yet been isolated. A. H.

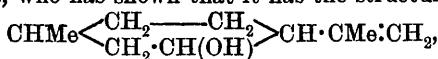
**Oil of Neroli.** By HEINRICH WALBAUM (*Ber.*, 1899, 32, 1512. Compare E. and H. Erdmann, preceding abstract).—The author claims priority for the observation that oil of orange-blossom contains methylic anthranilate. M. O. F.

**Essential Oil of Thyme.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 1009—1011).—From oil of thyme, 30 per cent. of thymol was extracted by treatment with aqueous potash, and the insoluble portion of the oil, on fractional distillation, yielded (1) 17 per cent. of a hydrocarbon boiling at 156—158°, which differs from pinene in forming a nitrosochloride melting at 106·5° and not yielding a hydrochloride; (2) 15 per cent. of menthene; (3) 21 per cent. of cymene; (4) 5 per cent. of linalool; (5) 8 per cent. of borneol, and (6) 4 per cent. of a residue boiling above 230°, and including, among other products, a small quantity of carvacrol. N. L.

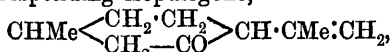
**Menthone from the Essence of Geranium from Bourbon.** By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 788—790).—The essential oil of geranium from Bourbon, after hydrolysis, is treated with phthalic anhydride to remove geraniol and citronellol (compare *Abstr.*, 1898, i, 618); the ketonic portion of the oil remains unaltered, and is extracted with ether and fractionated. The fraction boiling at 204—206° has an agreeable odour resembling that of menthone, the amount present in the original oil being about 6—7 per cent. The semicarbazone of this ketone is identical with that obtained from  $\alpha$ -menthone; it melts at 180°, and crystallises from alcohol in white prisms.  $\alpha$ -Menthone is most readily obtained from menthol by boiling this substance for 2 hours with potassium dichromate and 6 per cent. sulphuric acid; the oil is washed with water, extracted with ether, and fractionated. The semicarbazone is prepared by mixing together menthone, semicarbazide hydrochloride, and

potassium acetate in dilute alcohol. Lævo-menthone, obtained by Beckmann's method from the corresponding menthol, yields a semicarbazone melting at 184—184.5° which closely resembles its isomeride.  
G. T. M.

**Occurrence of Isopulegol in Commercial Citronellal.** By FERDINAND TIEMANN (*Ber.*, 1899, 32, 825—826).—The author and R. Schmidt have already proved (*Abstr.*, 1896, i, 383) that citronellal is readily converted into isopulegol. This substance has been studied by C. Harries, who has shown that it has the structure



and that the corresponding isopulegone,



exists in two stereoisomeric forms, of which one yields a semicarbazone which is sparingly soluble in ether and melts at 180°, and the other a semicarbazone which is more readily soluble in ether and melts at 171—172°, the mixture of the two semicarbazones melting at 173—174°.

When citronellal in commercial samples is separated from the accompanying terpenes by conversion into stable sodium citronellal-hydrosulphonate, a residue is obtained which has the odour, boiling point, and refractive index of isopulegol, but which probably contains, also, small quantities of geraniol and citronellol. The presence of isopulegol in the mixture was proved by oxidising it with chromic acid mixture, and converting the resulting isopulegone into the characteristic mixture of semicarbazones which melted at 173° and was separable into two portions having the properties described above. A. L.

**Separation of Citral and Citronellal.** By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 1012—1013).—The process recommended for the separation of the two aldehydes depends on the fact that when barium chloride is added to the aqueous solution of their mixed sodium hydrogen sulphite derivatives, the whole of the citral remains in solution, whilst the citronellal is quantitatively precipitated as the corresponding barium derivative,  $\text{C}_{20}\text{H}_{38}\text{O}_8\text{S}_2\text{Ba}$ . This is a white powder, insoluble in cold water and organic solvents, and only partially decomposed by boiling water, alkalis, and dilute acids; the citronellal may be recovered from it by treatment with 10 per cent. alcoholic potash. N. L.

**Separation of Citral from Citronellal and Methylheptenone.** By FERDINAND TIEMANN (*Ber.*, 32, 1889, 812—823).—Flatau and Labbé (preceding abstract and *Bull. Soc. Chim.*, 1899, [iii], 21, 77) have proposed a method of separation in which a solution of the sodium hydrogen sulphite compounds of the two aldehydes is treated with barium chloride; the barium hydrogen sulphite derivative of citronellal is said to be precipitated, whilst the citral remains in solution. The author finds that the citronellal is not completely precipitated, and that the precipitate contains citral; moreover, neither aldehyde can be regenerated from the solution or precipitate without considerable loss.



It is found that citral is dissolved as the labile sodium citral-dihydrodisulphonate (compare this vol., i, 248) by a dilute solution of sodium sulphite containing sodium hydrogen carbonate, and can be regenerated from this solution with caustic soda; citronellal is not affected by this solution. Further, a concentrated solution of sodium hydrogen sulphite containing sodium hydrogen carbonate dissolves citral, as the dilute solution does, but converts citronellal into the insoluble sodium hydrogen sulphite compound; and, when shaken with a fairly strong solution of sodium sulphite while a current of carbonic anhydride is passed through, citral dissolves as before, and citronellal also dissolves, but as stable sodium citronellalhydro-sulphonate, which is not decomposed by caustic soda.

All these methods may be used for separating citral from citronellal. Perhaps the best method, available also in the presence of methylheptenone, terpene alcohols and terpenes, is first to shake the oil with a solution containing 100 grams of  $\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$  and 35 grams of  $\text{NaHCO}_3$  in 1 litre of water; this dissolves the citral, which can be liberated from the solution by means of caustic soda. The oil is next shaken with a solution of 350 grams of  $\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$  and 62.5 grams of  $\text{NaHCO}_3$  in 1 litre of water; a precipitate is formed of the sodium hydrogen sulphite compound of citronellal, from which the citronellal can be liberated by means of sodium carbonate. The residual oil, extracted with ether from the crystals and aqueous solution, is shaken with a solution of 1 part of commercial solid sodium hydrogen sulphite in  $1\frac{1}{2}$  parts of water, the solution being cooled with ice; in these circumstances, the sodium hydrogen sulphite compound of methylheptenone is precipitated; this yields methylheptenone when treated with sodium carbonate.

It is found that oil of lemon-grass contains 0.2 and oil of lemons 0.4 per cent. of citronellal.

C. F. B.

**Natural Citral and the Composition of Oil of Lemon Grass.** By FERDINAND TIEMANN (*Ber.*, 1899, 32, 830—835).—The richest source of citral is oil of lemon grass, which contains 73—82 per cent. of citral, and little of other aldehydes. Citronellal and methylheptenone are also present and may be isolated as described in the preceding abstract. The residual oil contains 5—6 per cent. of terpenes (limonene, dipentene, sesquiterpenes, &c.), and also terpene alcohols (geraniol, and probably *l*-linalool and *l*-terpineol). By treatment with alcoholic potash, followed by distillation with steam and fractionation of the oil that distils over, methylheptenone and crude geraniol were obtained. Geraniol can also be obtained directly from oil of lemon-grass by treatment with benzoic anhydride and hydrolysis of the benzoates formed; in this way, Schimmel and Co. have prepared it on the large scale during the last few years.

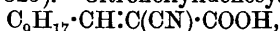
C. F. B.

**Stiehls Three Lemon Grass Aldehydes.** By FERDINAND TIEMANN (*Ber.*, 1899, 32, 827—830).—It has already been shown that citriodorlaldehyde and citral are identical (this vol., i, 247), and now Stiehls experiments (this vol., i, 66) have been repeated step by step and determinations made of the physical constants of the aldehydic portions of the fractions termed citral and allolemonal, and also of

the so-called citriodoralddehyde; moreover, the melting points of the derived semicarbazones, citralidinecyanacetic acids, and  $\beta$ -naphthacinchonic acids as well as the physical constants of the pseudoionones and ionones obtained from each have also been observed. The results entirely confirm Semmler's and Doebner's conclusions (this vol., i, 223) and show that citriodoralddehyde, citral, and allolemonal are identical.

Stiehl has endeavoured to show that the sodium hydrogen sulphite compounds of the three fractions have different properties; this view does not bear investigation. The double compounds may be purified in a simple manner by means of a solution of common salt, which dissolves the admixed sodium sulphite and hydrogen sulphite, and the residue becomes microcrystalline, proving in each case to be the normal sodium hydrogen sulphite compound of citral. A. L.

**Citronellylidenecyanacetic Acid.** By FERDINAND TIEMANN (*Ber.*, 1899, 32, 824—825).—Citronellylidenecyanacetic acid,

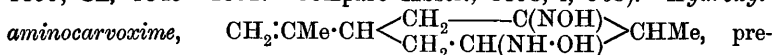


prepared by shaking citronellal with a solution of cyanacetic acid and sodium hydroxide in water, crystallises from benzene or alcohol in tabular crystals, melts at 137—138°, and is insoluble in water, but dissolves readily in alcohol and ether. Its acidic properties are less marked than those of citralidenecyanacetic acid. The *sodium* salt is sparingly soluble, and is especially characteristic; it separates in crystals on allowing the solution of the acid in moderately dilute warm soda to cool, whilst the salt of citralidenecyanacetic acid remains in solution under these conditions. The neutral solution of the ammonium salt gives nearly white precipitates with calcium chloride, copper acetate, and lead salts.

The detection of citral by means of citralidenecyanacetic acid is not rendered useless by the presence of citronellal in the oil, as the crude cyanacetic acid on recrystallisation from a mixture of benzene and alcohol gives without difficulty the pure citralidene derivative melting at 122°. A. L.

**Transformations in the Carvone Series.** By AUGUST KLAGES (*Ber.*, 1899, 32, 1516—1521).—When carvone is heated with formic acid in a reflux apparatus, carvacrol is produced quantitatively; the same agent converts dihydrocarvone into carvenone. M. O. F.

**Hydroxylaminocarvoxime, and its Conversion into Dihydrocarvyldiamine.** By CARL D. HARRIES and F. MAYRHOFER (*Ber.*, 1899, 32, 1345—1352. Compare *Abstr.*, 1898, i, 568).—*Hydroxylaminocarvoxime*,



prepared by the action of hydroxylamine dissolved in methylic alcohol on carvone at ordinary temperatures, melts somewhat indefinitely at 60—65°, a specimen on one occasion melting at 83—84°; it boils at 190° under 6—7 mm. pressure, and a small quantity may be distilled under reduced pressure without decomposing, but large quantities decompose explosively. The *dibenzoyl* derivative crystallises from absolute alcohol, and melts at 171—172°; the *diphenylcarbimide* and *diphenylthiocarbimide* derivatives melt at 96—97° and 142—143° respectively.

The *dioxime*,  $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{C}(\text{NOH})\\ \text{CH}_2\cdot\text{C}(\text{NOH})\end{smallmatrix}\right\rangle\text{CHMe}$ , obtained in an impure form by Wallach and Schrader (Abstr., 1894, i, 536), crystallises from absolute alcohol, melts and decomposes at  $193\text{--}194^\circ$  when rapidly heated, and at  $188^\circ$  when the temperature is raised more slowly; it reduces Fehling's solution, and when treated with boiling dilute sulphuric acid, yields the diketone melting at  $194^\circ$ . The *dibenzoyl* derivative melts and decomposes at  $118\text{--}120^\circ$ . The mother liquors of the dioxime yield an isomeric compound,  $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2$ , which melts indefinitely at  $153\text{--}155^\circ$ .

*Dihydrocarvyldiamine*,  $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}\left\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}(\text{NH}_2)\\ \text{CH}_2\cdot\text{CH}(\text{NH}_2)\end{smallmatrix}\right\rangle\text{CHMe}$ , prepared by reducing hydroxylaminocarvoxime with sodium and alcohol, boils at  $258\text{--}260^\circ$  under atmospheric pressure, and at  $122\text{--}123^\circ$  under 10 mm.; it is a colourless, optically inactive liquid with a basic odour, and readily absorbs carbonic anhydride from the atmosphere. The *hydrochloride* is hygroscopic, and the *oxalate* forms a white powder melting at  $135\text{--}140^\circ$ ; the *aurechloride* crystallises in long needles, and the *picrate* begins to char at  $229^\circ$ , intumescing at  $250^\circ$ . The *dibenzoyl* derivative melts at  $275\text{--}276^\circ$ ; the *diphenylcarbamide* and *diphenylthiocarbamide* derivatives melt at  $214\text{--}216^\circ$  and  $179\text{--}180^\circ$  respectively.

When dihydrocarvyldiamine hydrochloride is submitted to dry distillation, a *hydrocarbon* is produced isomeric with cymene; it boils at  $170\text{--}175^\circ$ , and decolorises bromine and potassium permanganate.

M. O. F.

**Racemisation of Camphor.** By A. DEBIERNE (*Compt. rend.*, 1899, 128, 1110—1113).—Anhydrous aluminium chloride is added to a cooled solution of camphor in toluene, and the mixture heated at  $80\text{--}85^\circ$  for 15 hours; the product, which has become optically inactive, is then poured into water, the supernatant oil distilled with steam, and the oily distillate rectified until all the toluene is removed; the residue, which solidifies on cooling, is crystallised from alcohol. The final product has all the properties of camphor, but is optically inactive; on oxidation with nitric acid, it yields an inactive camphoric acid which melts at  $208^\circ$ . This substance is shown to be a racemic compound by resolving it into its active components by means of cinchonine, and also by comparing it with the inactive acid prepared by mixing equal parts of dextro- and lævo-rotatory camphoric acids. It follows from this that the inactive camphor produced by the action of aluminium chloride is a racemoid modification of dextro- and lævo-camphor.

G. T. M.

**Physical Properties of some Camphors and Allied Substances.** By JULIUS W. BRÜHL (*Ber.*, 1899, 32, 1222—1236).—The density, molecular volume, refractive index for six wave-lengths, molecular refraction and dispersion, and heat of combustion are given for a number of oxygen compounds of the terpene series. In accordance with its labile nature, carvone has a higher heat of combustion, a greater molecular volume, and a lower molecular refraction and dispersion than carvacrol. Similarly, tanacetone has a greater molecular

volume and a lower molecular refraction and dispersion than carvotanacetone. In the series carone-dihydroeucarvone-dihydrocarvone-carvenone, carone has the highest heat of combustion and carvenone the lowest, corresponding with the order of stability of the four compounds; similarly, carone has the lowest and carvenone the highest molecular refraction; carvenone has also the highest molecular dispersion, those of the other three compounds being smaller and nearly equal; on the other hand, carone, although the most labile member of the series, has the lowest molecular volume, those of the other three compounds being larger and nearly equal to one another. The constants of dihydrocarvone and dihydroeucarvone are very similar, in spite of the wide difference between the formulæ assigned to them.

An examination of the constants of trimethylenecarboxylic and tetramethylenecarboxylic acids shows that the increments of molecular volume, molecular refraction, and molecular dispersion are very similar to those in the case of homologues of the aliphatic series.

The degree of saturation of the various compounds can be calculated from the physical constants. Carvone and carvacrol give numbers corresponding closely with the formulæ  $C_{10}H_{14}O''|_{=2}$  and  $C_{10}H_{14}O'|_{=3}$  respectively. The numbers for tanacetone are somewhat higher than those corresponding with the formula  $C_{10}H_{16}O''$ , and it is possible that a part of the substance has the enolic form  $C_{10}H_{16}O'|_{=}$ . Carvotanacetone also gives numbers higher than those corresponding with  $C_{10}H_{16}O''|_{=}$ . Dihydrocarvone and dihydroeucarvone give numbers corresponding with the ketonic formula  $C_{10}H_{16}O''|_{=}$ , but the values for carone and carvenone agree closely with those for the enolic formulæ  $C_{10}H_{16}O'|_{=}$  and  $C_{10}H_{16}O'|_{=2}$ . T. M. L.

**Derivatives of Amidocamphor.** By PAUL DUDEN and W. PRITZKOW (*Ber.*, 1899, 32, 1538—1543).—Amidocamphor is conveniently prepared by reducing isonitrosocamphor with zinc dust and caustic soda; the *hydrogen oxalate* crystallises from alcohol in leaflets melting at 194°. The *picrate* forms long needles and decomposes at 191°, whilst the *hydriodide* separates from water in beautiful, flattened needles and melts at 252—253°, when it decomposes.

*Methylamidocamphor*,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NHMe} \\ | \\ \text{CO} \end{smallmatrix}$ , is a pale yellow oil which boils at 241° under 746 mm. pressure, and solidifies in a freezing mixture; it is indifferent towards Fehling's solution, and does not undergo condensation with benzaldehyde or ethylic acetoacetate. The *hydrochloride* crystallises in prisms, and becomes brown when heated, melting and decomposing at 228°; the *hydriodide*, *hydrogen oxalate*, and *picrate* melt at 201—202°, 191°, and 187° respectively. The *nitrosamine* crystallises from alcohol in six-sided prisms and melts at 78°, whilst the *acetyl* derivative forms colourless leaflets melting at 105°; the *carbamide* derivative crystallises from alcohol in small, rectangular plates and melts at 185°. *Methylamidoborneol*,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NHMe} \\ | \\ \text{CH} \cdot \text{OH} \end{smallmatrix}$ , obtained by reducing methylamidocamphor in alcohol with sodium, boils at 257—258° under 744 mm. pressure.

Dimethylamidocamphor,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NMe}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , crystallises from petroleum and melts at  $37^\circ$ , boiling at  $242\text{--}243^\circ$  under 745 mm.; the *hydrochloride* melts at  $220\text{--}222^\circ$ , whilst the *hydriodide* and *picrate* melt at  $243^\circ$  and  $213^\circ$  respectively. The *methiodide* crystallises in four-sided plates melting at  $206^\circ$ , and the corresponding *platinochloride* forms small, orange-coloured crystals which melt and decompose at  $228^\circ$ .

Dimethylamidoborneol,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NMe}_2 \\ | \\ \text{CH} \cdot \text{OH} \end{smallmatrix}$ , prepared by reducing dimethylamidocamphor in alcoholic solution with sodium, crystallises from light petroleum in small prisms and melts at about  $80^\circ$ ; it boils at  $259\text{--}261^\circ$  under 755 mm. pressure. M. O. F.

**Camphenilone.** By WILHELM JAGELKI (*Ber.*, 1899, 32, 1498—1511).—Oxidation of camphene with dilute nitric acid leads to camphoic acid (Marsh and Gardner, *Trans.*, 1891, 59, 648; 1896, 69, 74), a compound which has been called *carboxylapocamphoric acid* by Brecht and Jagelki (*Chem. Zeit.*, 1896, 20, 842). In addition to the substance mentioned, there are formed dehydrocamphenylic acid,  $C_{10}H_{14}O_2$ , and the ketone, camphenylone, described by Majewski and Wagner (this vol. i, 629); camphenilic nitrite is the remaining product which has been isolated.

*Camphenilic nitrite*,  $\begin{smallmatrix} \text{CH}_2\text{—CH—} \\ | \qquad \qquad \qquad \diagup \\ \text{CH}_2\text{—CMe—} \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{O} \cdot \text{NO} \end{smallmatrix}$ , melts at  $66^\circ$ ,

and boils at  $147^\circ$  under 12 mm. pressure; it crystallises from petroleum in pale yellow needles, and detonates when heated strongly. Warm, concentrated sulphuric acid develops a beautiful, cherry-red coloration. Reduction with tin and hydrochloric acid or with zinc dust and acetic acid converts it into camphenilanaldehyde, obtained by Brecht and Jagelki on oxidising camphene with chromyl chloride (*loc. cit.*). Oxidation with potassium permanganate, or treatment with alcoholic potash, gives rise to camphenylone, which the authors call *camphenilone*.

The production of camphenilic nitrite depends on the initial formation of camphene nitrosite, arising from addition of the elements of nitrous acid to camphene; this is established by a study of the behaviour of the hydrocarbon towards nitrous acid, which gives rise to the two following substances along with camphenilic nitrite.

Camphene *nitronitrosite*,  $C_8H_{14} \begin{smallmatrix} \text{C}(\text{NO}) \cdot \text{NO}_2 \\ | \\ \text{CH} \cdot \text{NO}_2 \end{smallmatrix}$ , is a colourless substance which becomes blue when heated, and decomposes at  $149^\circ$ , yielding water and oxides of nitrogen; it is insoluble in common media, but forms a blue solution in nitrobenzene. Camphene *nitrosite*,

$C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NO} \\ | \\ \text{CH} \cdot \text{NO}_2 \end{smallmatrix}$ , is an oil which decomposes when heated under reduced pressure at  $50^\circ$ , yielding water, nitrous oxide, and camphenilic nitrite; the *potassium* derivative separates from alcohol in red crystals which detonate when heated, and the *benzoyl* derivative is a greenish-yellow, viscous liquid which cannot be distilled.

Camphenilone yields the *semicarbazone* in white crystals which melt

and decompose at 220—222°. The *hydrochloride* of the oxime is a white powder, and the *hydrobromide* is yellow; the *platinochloride* crystallises from alcohol in yellow needles and melts at 106°.

*Camphenilol*,  $\text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}(\text{OH}) \\ \diagdown \quad \diagup \\ \text{CMe}_2 \end{array} \text{CH}$ , prepared by reducing the ketone

with sodium in alcohol, crystallises in lustrous leaflets and melts at 84°; it boils at 88.5—89° under 11 mm. pressure.

*Camphenilone pinacone*,  $\text{C}_{18}\text{H}_{30}\text{O}_2$ , obtained on reducing an ethereal solution of the ketone, crystallises in plates and melts at 134°; it boils at 200—202° under 11 mm. pressure.

*Camphenilylic chloride*,  $\text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CHCl} \\ \diagdown \quad \diagup \\ \text{CMe}_2 \end{array} \text{CH}$ , produced on treating

camphenilol with phosphorus pentachloride, is a white, volatile substance resembling camphene; it melts at 50°, and boils at 73° under 11 mm. pressure.

*Camphenilene*,  $\text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}=\text{C} \\ \diagdown \quad \diagup \\ \text{CMe}_2 \end{array}$ , is formed by the elimination of

hydrogen chloride from camphenilylic chloride by the agency of aniline at 175°; it is a colourless liquid which boils at 142°, and decolorises solutions of bromine and of potassium permanganate.

When campheniloneoxime is oxidised with potassium permanganate, a considerable proportion of the ketone is regenerated, but on heating the substance with dehydrating agents, it loses the elements of water, and gives rise to a nitrile.

*Camphoceanic nitrile*,  $\begin{array}{c} \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{CMe} \cdot \text{CMe}_2 \end{array} > \text{CH} \cdot \text{CN}$ , prepared by the action of acetic chloride on campheniloneoxime, is a colourless oil which boils at 95—100° under 15 mm. pressure; it instantly decolorises bromine and potassium permanganate. *Isocampheniloneoxime*,  $\text{C}_9\text{H}_{15}\text{NO}$ , a bye-product in the conversion of the oxime into nitrile, crystallises from alcohol in plates and melts at 165°; the *platinochloride* is a yellow powder.

*Camphoceanic acid*,  $\begin{array}{c} \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{CMe} \cdot \text{CMe}_2 \end{array} > \text{CH} \cdot \text{COOH}$ , produced on hydrolysing the nitrile or the amide, melts at 54°, and boils at 145° under 14 mm. pressure; it instantly decolorises bromine and potassium permanganate. The *calcium* salt forms slender needles, and the *sodium* salt contains  $1\frac{1}{2}\text{H}_2\text{O}$ ; the *silver* salt is sensitive towards light, and the *copper* salt forms a green powder soluble in chloroform. The *amide* crystallises from alcohol in lustrous leaflets and melts at 155°, when it decomposes; it boils at 145°.

*Dihydroxycamphoceanic acid*,  $\begin{array}{c} \text{OH} \cdot \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{OH} \cdot \text{CMe} \cdot \text{CMe}_2 \end{array} > \text{CH} \cdot \text{COOH}$ , prepared by oxidising a solution of sodium camphoceanate with 1 per cent. potassium permanganate, separates from alcohol in white, transparent crystals, and melts at 163°, losing water at 186°.

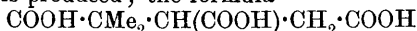
*Camphoceanic acid*,  $\begin{array}{c} \text{CO} - \text{CH}_2 \\ | \quad | \\ \text{CHMe} \cdot \text{CMe}_2 \end{array} > \text{CH} \cdot \text{COOH}$ , passes over at 184°

under 15 mm. pressure when dihydroxycamphoceanic acid is distilled, and forms white, lustrous crystals melting at  $173^{\circ}$ ; the oxime crystallises from alcohol in long needles and melts at  $150-156^{\circ}$ , when it decomposes.



undissolved when the product of distilling dihydroxycamphoceanic acid is treated with sodium carbonate; it melts at  $58^{\circ}$ , and boils at  $165^{\circ}$  under 13.5 mm. pressure.

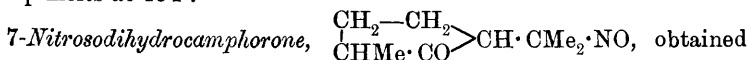
When camphoceanic acid is oxidised with potassium dichromate and sulphuric acid instead of with potassium permanganate, dimethyltricarballic acid is produced; the formula



represents the constitution of this compound (compare von Baeyer, Abstr., 1897, i, 82). M. O. F.

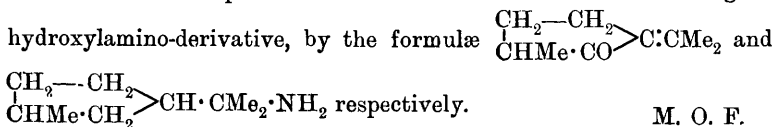
**Constitution of Camphorone.** By CARL D. HARRIES and ISRAEL MATFUS (*Ber.*, 1899, 32, 1343—1345. Compare Kerp, Abstr., 1896, i, 447).—*Camphoronehydroxylamine*,  $\begin{array}{c} \text{CH}_2\text{—CH}_2 \\ | \quad | \\ \text{CHMe·CO} \end{array} \text{CH·CMe}_2\text{·NH·OH}$ ,

prepared by heating camphorone with ether, alcohol, and hydroxylamine in a reflux apparatus, melts at  $119-120^{\circ}$  and is identical with camphoroneoxime described by Koenigs and Eppens (Abstr., 1893, i, 361), and later by Kerp (*loc. cit.*); it reduces Fehling's solution when moderately heated, and develops a blue coloration with yellow mercuric oxide, indicating that the hydroxylamino-group has become attached to a tertiary carbon atom at the double linking, and occupies the  $\beta$ -position to the carbonyl radicle. The oxalate mentioned by Kerp melts at  $154^{\circ}$ .



by oxidising camphoronehydroxylamine with sulphuric acid and potassium dichromate, sinters at  $73^{\circ}$  and melts at  $80-82^{\circ}$ , becoming blue; it dissolves readily in concentrated sulphuric and nitric acids, evolving gas.

In view of the results of these experiments, the authors express the constitution of camphorone and of the amine obtained on reducing its



**Camphenylic Acid and its Derivatives.** By J. MAJEWSKI and GEORG WAGNER (*Chem. Centr.*, 1897, i, 1056; from *J. Russ. Chem. Soc.*, 1896, 29, 124—132).—*Dehydrocamphenylic acid*,  $\text{C}_{10}\text{H}_{14}\text{O}_2$ , obtained from camphenylic acid by dehydration, crystallises in rhombohedral plates and melts at  $147.5-148^{\circ}$ ; it is indifferent towards potassium permanganate, and is therefore regarded by the authors as a derivative of the class of substances called tricyclenes (this vol., i, 618).

*Camphenylone*,  $\text{C}_9\text{H}_{14}\text{O}$  (compare Jagelki, this vol., i, 627), produced

on oxidising camphenylic acid with lead peroxide, melts at 36—38° and boils at 195° under 738 mm. pressure; it is indifferent towards an alkaline solution of potassium permanganate. Hot 40 per cent. nitric acid slowly oxidises the ketone, yielding oxalic acid along with an acid which melts at 114°. The *oxime* melts at 105—106°.

The *sodium* and *barium* salts of camphenylic acid crystallise in needles containing 1H<sub>2</sub>O, which is removed at 110°.

The constitution of the diketone from which camphenylic acid is obtained is expressed by the formula  $\text{CH}_2 \begin{array}{c} \text{CH} \text{---} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CMe} \quad \text{CMe}_2 \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{CO} \quad \text{CO} \end{array}$ , whilst

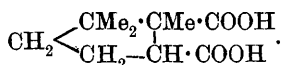
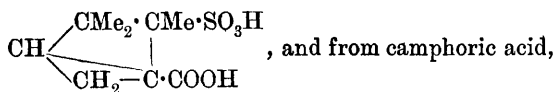
camphenylic acid and camphenylone are represented by the formulæ

$\text{CH}_2 \begin{array}{c} \text{CMe} \quad \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CMe} \quad \text{CMe}_2 \end{array} \text{C(OH) \cdot COOH}$  and  $\text{CH}_2 \begin{array}{c} \text{CMe} \quad \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{CMe} \quad \text{CMe}_2 \end{array} \text{CO}$  respectively. M. O. F.

**Constitution of Isolaurnolic Acid.** By G. BLANC (*Bull. Soc. Chim.*, 1898, 19, [iii], 699—706. Compare this vol., i, 536).—The author gives another demonstration of his constitutional formula for isolaurnolic acid. This substance, when heated in sealed tubes at 300° for 4 hours, decomposes quantitatively into carbonic anhydride and an inactive hydrocarbon, C<sub>8</sub>H<sub>14</sub>, boiling at 108·5° under 758 mm. pressure. This compound is identical with the substance obtained by Damsky (Abstr., 1888, 293) and Koenigs and Meyer (Abstr., 1895, i, 155) from sulphocamphylic acid and by Moitessier from copper camphorate; it differs from the product derived from camphanic, lauronolic, and  $\alpha$ -camphoramic acids, which is active and boils at 120°. The inactive hydrocarbon, when treated with a 1 per cent. solution of permanganate, yields dimethylhexanonic acid, COMe·CMe<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·COOH, and this, on further oxidation with sodium hypobromite, gives rise to  $\alpha$ -dimethylglutaric acid. This result shows that the hydrocarbon possesses the constitution  $\text{CMe}_2 \begin{array}{c} \text{CMe} \cdot \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ , and as it is derived from inactive lauronolic acid by loss of carbonic anhydride, it follows that the carboxyl group of this acid must be attached to carbon atom 3.

Moreover, the inactive hydrocarbon, when dissolved in carbon bisulphide and treated with acetic chloride in the presence of aluminium chloride, yields a ketone identical with that obtained from isolaurnolic chloride with zinc methyl; the substance is further identified by means of its semicarbazone, which melts at 230—232° and not at 49° as previously stated (compare Abstr., 1897, i, 554). Since the entrant acetyl group certainly attaches itself to the carbon atom 3, the ketone must have the formula  $\text{CMe}_2 \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{COMe} \\ \diagdown \quad \diagup \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ , and as the ketone is also obtained from isolaurnolic chloride, it follows that isolaurnolic acid must have the constitution  $\text{CMe}_2 \begin{array}{c} \text{CMe} \cdot \text{C} \cdot \text{COOH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ . This view of the constitution of the inactive hydrocarbon explains its formation from sulphocamphylic acid,





If Bouveault's formula for camphoric acid is correct, the active hydrocarbon boiling at  $120^\circ$  must have a constitution represented by the formula  $\text{CH}_2 \begin{cases} \text{CMe}_2 \cdot \text{CHMe} \\ \text{CH} = \text{CH} \end{cases}$ , as it is also derived from this acid.

G. T. M.

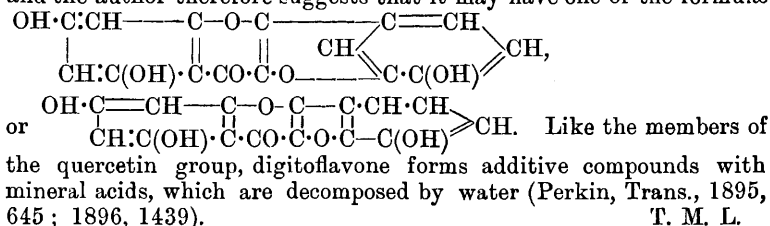
**Oximes of Methylic Santonate and their Optical Behaviour.** By EDGAR WEDEKIND (*Ber.*, 1899, 32, 1411—1415).—When santonin-oxime, melting at  $216$ — $217^\circ$ , is reduced with aluminium amalgam in alcoholic solution to which a little water has been added, a resinous product is obtained which melts at  $180^\circ$ . When the oxime is heated at  $220^\circ$  until the evolution of gas slackens, santonin is obtained, hydroxylamine having been eliminated through the agency of one of the molecules of water of crystallisation.

When methylic santonate in alcoholic solution is heated with hydroxylamine hydrochloride and chalk for several hours at  $75^\circ$ , the product poured into water and extracted with ether, and the ethereal extract concentrated and mixed with alcohol, two substances,  $\text{C}_{16}\text{H}_{23}\text{NO}_4$ , crystallise. The one which separates first, termed the  $\alpha$ -oxime, is formed in much larger amount; it crystallises in tetrahedra, melts at  $158$ — $159^\circ$ , has a specific rotation  $[\alpha]_D - 40.66^\circ$  in 1.5 per cent. alcoholic solution at  $26^\circ$ , and, when boiled with very dilute sulphuric acid, dissolves, yielding a solution which has a specific rotation  $[\alpha]_D + 42.5^\circ$  (in 1.6 per cent. solution) after boiling for 3 hours. The  $\beta$ -oxime melts at  $193$ — $194^\circ$  and crystallises, with  $1\text{H}_2\text{O}$ , in needles; it has a specific rotation  $+18.15^\circ$  in 0.826 per cent. alcoholic solution at  $19^\circ$ , and about  $+72^\circ$  after boiling with dilute sulphuric acid.

C. F. B.

**Digitoflavone, a New Substance Isolated from Digitalis Purpurea.** By FRANZ FLEISCHER (*Ber.*, 1899, 32, 1184—1190).—*Digitoflavone*,  $\text{C}_{15}\text{H}_{10}\text{O}_6 + \text{H}_2\text{O}$ , isolated from the leaves of *Digitalis purpurea*, separates from 70 per cent. alcohol in yellow crystals, becomes anhydrous at  $150^\circ$ , and melts when rapidly heated to  $320^\circ$ , but if heated gradually chars at  $300^\circ$ ; it dissolves in acetone and acetic acid, and less rapidly in ether, but is only very slightly soluble in boiling water. It is not a glucoside, does not interact with phenylhydrazine, and does not contain any methoxy-groups, but behaves as a trivalent phenol. The *tribenzoate* forms small, colourless needles, and melts at  $219^\circ$ , is insoluble in water, and only slightly soluble in alcohol; the molecular weight in naphthalene solution is normal. The *triacetate* crystallises in colourless needles, melts at  $221$ — $222^\circ$ , and dissolves in alcohol, acetic acid, ether, or chloroform. The *tribenzenesulphonate* crystallises from a mixture of chloroform and ether in slender, colourless needles, and melts at  $189^\circ$ . The formula corresponds with that of a flavone derivative, and this conclusion is

supported by the formation of phloroglucinol and an acid, which is probably protocatechuic acid, on heating the substance with alkalis. There are therefore two hydroxyl groups in the 2 : 4 positions, but the orientation of the third and the nature of the remaining oxygen atom have not been definitely established. On heating the substance with concentrated hydrochloric acid at 350°, catechol appears to be formed, and the author therefore suggests that it may have one of the formulæ

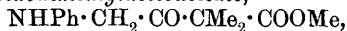


**4 : 4-Dimethyl-3-keto-5-pyrrolidone and its Derivatives.** By MAX CONRAD and KARL HOCK (*Ber.*, 1899, 32, 1199—1208).—Alcoholic ammonia converts methylic bromodimethylacetoacetate into

4 : 4-dimethyl-3-keto-5-pyrrolidone,  $\text{NH} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} - \text{CMe}_2 \end{array}$ , which forms large, well-developed crystals melting at 144°. The *monoxime* melts at 230°, and the *phenylhydrazone* crystallises in long, white prisms melting at 168°. Dimethylketopyrrolidone is converted by boiling with hydrochloric acid into *amidomethyl isopropyl ketone* (amidodimethylacetone) *hydrochloride*,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot \text{HCl}$ , which crystallises in nacreous, white scales melting at 165°. The base is a heavy oil which has strongly reducing properties, and has not yet been obtained in a pure state. The hydrochloride reacts with phenylhydrazine yielding isopropylphenylglyoxalosazone. Potassium cyanate converts the hydrochloride into *isopropylimidazolone*,  $\text{CHMe}_2 \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \end{array}$ , which melts

at 220°. When amidomethyl isopropyl ketone hydrochloride is boiled with aqueous soda and mercuric chloride, it yields 2 : 5-di-isopropylpyrazine,  $\begin{array}{c} \text{CH} - \text{N} \cdot \text{CPr}^\beta \\ | \qquad | \\ \text{CPr}^\beta \cdot \text{N} \cdot \text{CH} \end{array}$ , which is a colourless, highly refractive liquid with an odour like that of jasmine, boils at 206—207°, and has a sp. gr. 0.924 at 15°. On reduction, it is converted into *di-isopropylpiperazine*,  $\text{CHMe}_2 \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CHMe}_2$ , which is colourless and crystalline, melts at 58°, boils at 234°, and forms a strongly alkaline solution in water. The *urate* forms lozenge-shaped crystals, and the *hydrochloride*,  $\text{C}_{10}\text{H}_{22}\text{N}_2 \cdot 2\text{HCl}$ , melts at 220°. *Nitrosoimido-bisdimethylacetone*,  $\text{NO} \cdot \text{N}(\text{CH}_2 \cdot \text{CO} \cdot \text{CHMe}_2)_2$ , is obtained from the mother liquors from the preparation of dimethylketopyrrolidone, and crystallises in colourless needles melting at 112°.

Aniline readily reacts with methylic bromodimethylacetoacetate, forming *ethylic anilidodimethylacetoacetate*,



which melts at 64°. At 160—180°, this compound loses the elements of

methylic alcohol, and is converted into 1-phenyldimethylketopyrrolidone,  $\text{NPh} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CMe}_2 \end{array}$ , which forms colourless crystals, melts at  $104^\circ$ , and boils at  $315\text{--}316^\circ$ . The *monoxime* crystallises in lustrous, white prisms melting at  $168^\circ$ , and the *phenylhydrazone* in colourless plates melting at about  $196^\circ$ . Methoxyaniline and ethoxyaniline react in a similar manner to aniline with methylic bromodimethylacetate; *orthomethoxyphenyldimethylketopyrrolidone*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{CMe}_2 \end{array}$ , forms colourless crystals melting at  $132^\circ$ , whilst the corresponding *ethoxy*-compound melts at  $130^\circ$ .  
A. H.

**Carboxylic Acids of Pyrrolidine.** By RICHARD WILLSTÄTTER and WALTHER VON SICHERER (*Ber.*, 1899, 32, 1290—1293).— $\beta$ -Methyladipic acid, which is best obtained by the oxidation of pulegone with potassium permanganate, is readily brominated by Volhard's method, forming *ethylic*  $\alpha_1\alpha_2$ -dibromo- $\beta$ -methyladipate,  $\text{C}_2\text{H}_4(\text{CHBr} \cdot \text{COOEt})_2$ , a colourless, strongly refractive oil which boils at  $202\text{--}204^\circ$  or at  $182\text{--}183^\circ$  under pressures of 24 or 9 mm. respectively, and is converted on heating in a closed tube at  $140^\circ$  for 5 hours with methyl alcoholic ammonia into 3-methylpyrrolidine-2:5-dicarboxylic acid, a colourless substance separating from alcohol in needles, melting and decomposing at  $239^\circ$ , and closely resembling hygric and tropic acids in its properties; the *platinochloride* separates from its aqueous solution in characteristic plates which decompose without melting when heated, and the *silver* salt is obtained from its aqueous solution on the addition of alcohol as a flocculent precipitate.  
J. F. T.

**Action of Chloranil on Pyridine.** By H. IMBERT (*Bull. Soc. Chim.*, 1898, [iii], 19, 1008—1009).—When tetrachloroquinone (1 mol.) is added in small quantities at a time to an alcoholic solution of pyridine (2 mols.) and the liquid heated in a reflux apparatus for 8—10 hours, a small quantity of a *substance*,  $\text{C}_6\text{O}_2(\text{C}_5\text{NH}_3)_2 + 3\text{H}_2\text{O}$ , is obtained which crystallises in slender, golden-yellow needles and is slightly soluble in cold, much more soluble in boiling, water and alcohol; it is not decomposed at  $105^\circ$ , but yields pyridine when distilled. Its aqueous solution gives an intense red-brown coloration with ferric chloride solution.  
N. L.

**Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1'-Alkylquinolones.** II. By OTTO FISCHER (*Ber.*, 1899, 32, 1297—1307).—The method previously described (*Abstr.*, 1898, i, 382) for the conversion of 1-alkylpyridones and 1'-alkylquinolones into halogen derivatives of pyridine and quinoline respectively by the action of the corresponding phosphorus haloid appears to be a general one.

[With W. HOERGER and R. JAEGER.]—2-Chloropyridine is best prepared by heating either 1-methyl-, 1-ethyl-, or 1-benzyl-pyridone mixed with phosphorus oxychloride with phosphorus pentachloride at  $150\text{--}170^\circ$ ; it has a sp. gr. 1.205 at  $15^\circ$ , and is readily reduced by sodium in alcoholic solution to piperidine. On heating for 20 hours with methylic iodide at  $100^\circ$ , it is converted into

*2-iodopyridine methiodide*, a colourless substance which separates from hot water in needles melting and decomposing at  $207^{\circ}$ ; this readily reacts with bases, forming with aniline  *$\alpha$ -anilidopyridine methiodide*, which crystallises from hot water in fine, white needles melting and decomposing at  $176$ — $179^{\circ}$ ; the *methochloride* formed from this by the action of silver chloride is obtained on evaporation of its aqueous solution as an oil which gradually solidifies and then melts at  $65^{\circ}$ . The *aurichloride* is a yellow, crystalline powder, and the *platinochloride* forms reddish-yellow needles melting at  $214^{\circ}$ . 2-Chloropyridine, when heated with zinc ammonium chloride for 5 hours at  $220^{\circ}$ , is quantitatively converted into 2-amidopyridine, which crystallises from light petroleum in leaflets melting at  $56^{\circ}$ , and when treated with potassium cyanate yields a sparingly soluble carbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_5\text{NH}_4$ , crystallising from moderately dilute alcohol in colourless prisms melting at  $195^{\circ}$ ; with carbon bisulphide in alcoholic solution, 2-amidopyridine yields *dipyridylthiocarbamide*,  $\text{CS}\cdot(\text{NH}\cdot\text{C}_5\text{NH}_4)_2$ , a colourless substance crystallising from hot water or from dilute alcohol in prisms melting at  $147^{\circ}$ . 2-Amidopyridine gives with aldehydes characteristic condensation products, thus with salicylaldehyde, an *orthohydroxybenzylidene* compound is formed which crystallises from alcohol in light yellow needles melting at  $69^{\circ}$ , and with paranitrobenzaldehyde, a *paranitrobenzylidene* derivative which melts at  $148^{\circ}$ ; these compounds are, however, very unstable.

2-Anilidopyridine, formed when 2-chloropyridine is heated with aniline zinc chloride in a sealed tube at  $200^{\circ}$ , is volatile in steam, and in that way is obtained in colourless leaflets melting at  $108^{\circ}$ ; the *aurichloride* forms red prisms and melts at  $149^{\circ}$ , whilst the *platinochloride* is a red, crystalline powder melting at  $202^{\circ}$ ; the *nitrosamine* crystallises in prisms melting at  $102^{\circ}$ .

1'-Benzylpyridone, which was mentioned as one of the substances from which 2-chloropyridine could be obtained, is best prepared by Decker's method from pyridine benzylochloride; it crystallises in colourless, glistening rhombohedra, and melts at  $75$ — $76^{\circ}$ ; the *mercurichloride* crystallises in white needles melting at  $124^{\circ}$ .

[With L. LEIDEL.]—2-Bromopyridine, which is prepared in the same way as the 2-chloro-derivative, is a highly refractive liquid having a sp. gr. 1.657 at  $15^{\circ}$ ; the *hydrochloride* crystallises in needles; the *platinochloride* forms fine, red needles, the *aurichloride* separates in yellow leaflets melting at  $173^{\circ}$ , and the *mercurichloride* crystallises in needles.

*Dibromopyridine*, which is a bye-product in this reaction, crystallises in white needles, melts at  $93^{\circ}$ , and gives a *platinochloride* forming red needles, an *aurichloride* consisting of yellow crystals, and a *mercurichloride* forming colourless needles sparingly soluble in water or alcohol. In the same way, 2'-bromoquinoline is obtained from 1'-methylquinoline on treatment with phosphorus pentabromide.

[With PAUL KLITZSCH.]—2'-Chloro-3-methylquinoline is prepared in an analogous way to 2'-chloroquinoline (Abstr., 1898, 382) from 3-methylquinoline. This substance, which has not been previously described, is prepared by Decker's method from 3-methylquinoline methiodide by oxidation with potassium ferricyanide and sodium

hydroxide; it crystallises in colourless plates and melts at  $90^{\circ}$ , the *picrate* forms silky, yellow needles, and the *hydrochloride* short, colourless needles; 2'-chloro-3-methylquinoline crystallises from dilute alcohol in long, colourless needles which melt at  $116^{\circ}$ ; the *hydrochloride* separates from alcoholic hydrogen chloride in long, colourless needles and is dissociated in water, and the *platinochloride* forms yellow leaflets. The chlorine atom in 2'-chloro-3-methylquinoline is readily replaceable, thus, with potassium hydrosulphide, 3-methylquinoline 2'-hydrosulphide is produced; it separates from hot alcohol or benzene in light yellow needles which melt at  $210^{\circ}$ ; its *methiodide* crystallises from a mixture of alcohol and ether in yellow needles, and it further forms a *methosulphide*, crystallising in colourless needles which melt at  $50^{\circ}$ . On treatment with hydrogen peroxide, the hydrosulphide is quickly converted into the *bisulphide*,  $C_{20}H_{16}N_2S_2$ , which crystallises from hot alcohol in colourless leaflets and melts at  $195^{\circ}$ .

Methyl- $\alpha$ -naphthaquinoline and methyl- $\beta$ -naphthaquinoline also react in the same way with phosphorus pentachloride, forming in the first instance  $\alpha$ -chlor- $\alpha$ -naphthaquinoline, a substance crystallising in needles and melting at  $105^{\circ}$ , and in the second, the corresponding  $\beta$ -derivative, which crystallises from alcohol in colourless, glistening needles, and melts at  $118^{\circ}$ .  
J. F. T.

Action of Phosphorus Pentachloride on 1-Alkylpyridones and 1'-Alkylquinolones. III. By OTTO FISCHER and KARL DEMELER (*Ber.*, 1899, 32, 1307—1311).—Alkyl-4-pyridones and acridones differ from the 2-derivatives (see preceding abstract) in their behaviour with phosphorus pentachloride, since the displacement of the alkylchloride takes place only at high temperatures, thus with phosphorus pentachloride 4-methylpyridine gives 4-chloropyridine methochloride, which is analogous to the formation of chlorophenylphenazonium chloride from aposaffranone, a behaviour which seems to show that these compounds have, as Claus has suggested, a betaine-like constitution. 4-Chloropyridine methochloride decomposes above  $200^{\circ}$  with formation of hydrogen chloride, methylic chloride, and 4-chloropyridine; it is an extremely hygroscopic substance, the *aurichloride* crystallises in golden-yellow needles melting at  $188$ — $190^{\circ}$ , and the *platinochloride* in reddish-yellow needles. The chlorine atom in  $\gamma$ -chloropyridine methochloride is very reactive, forming with aniline *anilidopyridine methochloride*, a substance which, although difficult to separate from aniline salts, forms a characteristic *aurichloride* crystallising in orange-coloured needles melting at  $133^{\circ}$ ; the *platinochloride* forms bright yellow needles which melt at  $197^{\circ}$ .

N-Methylacridone reacts with phosphorus pentachloride in the presence of phosphorus oxychloride to form  $\gamma$ -chloracridine methochloride, a hygroscopic substance melting at  $73^{\circ}$ ; its *aurichloride*, which melts at  $227^{\circ}$ , crystallises in orange-coloured needles, whilst the *platinochloride* forms a yellow, crystalline precipitate melting at  $224$ — $225^{\circ}$ .

With aniline,  $\gamma$ -chloracridine methochloride gives  $\gamma$ -anilidoacridine methochloride, a crystalline substance which separates from dilute alcohol in yellow silky prisms melting at  $235^{\circ}$ ; its *aurichloride* forms golden-yellow needles and melts at  $182$ — $183^{\circ}$ , and its *platinochloride*, red-yellow needles and melts at  $242^{\circ}$ ; the corresponding base, which

is free from oxygen, is precipitated as a yellow powder on the addition of ammonia to an alcoholic solution of the salt; it crystallises from alcohol in yellow needles melting at 162—163°, and evidently

possesses the constitutional formula  $\text{NMe} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \\ \text{N} \text{Ph} \\ \diagdown \text{C}_6\text{H}_4 \end{array} \text{CH}.$

*γ-Naphthalidoacridine methochloride*, from *γ*-chloracridine methochloride and *β*-naphthylamine, separates from dilute alcohol in red-yellow needles melting at 184—185°, and gives an *aurichloride* consisting of red-brown needles melting at 166—167° and a *platinochloride* forming brick-red octahedra which melt at 256°; the *base*, which crystallises from dilute alcohol in red needles and melts at 177°, must have a constitution analogous to that just indicated. J. F. T.

**Crystalline Form of Piperidine Hydrobromide and Methylallylaniline Picrate.** By EDGAR WEDEKIND (*Ber.*, 1899, 32, 1409—1411. Compare this vol., i, 449).—Piperidine hydrobromide crystallises in the rhombic system [ $a : b : c = 0.496 : 1 : 1.5282$ ], and shows no sign of hemihedry or hemimorphism. Methylallylaniline *picrate* (this vol., i, 353) forms hemihedral crystals of the monoclinic system [ $a : b : c = 1.3972 : 1 : 1.7437$ ]. C. F. B.

***α*- and *β*-Naphthaleneindigo.** By HERMANN WICHELHAUS (*Ber.* 1899, 32, 1236—1239. Compare Abstr., 1894, i, 42).—Better yields of the green indigo dyes previously described can be obtained by using Blank's method (Abstr., 1898, i, 589). Ethylic *β*-naphthylamidomalonate gives a yield of 83.5 per cent. of ethylic naphthylindoxylate melting at 157°, which when boiled with alkali, yields *β*-naphthaleneindigo, the yield being 54 per cent. of the theoretical. The dyeing properties of this compound with respect to colour and fastness are satisfactory. *α*-Naphthaleneindigo reacts with concentrated sulphuric acid at the ordinary temperature, yielding a *disulphonic acid*, which can be purified by solution in alcohol and precipitation with ether; under similar conditions *β*-naphthaleneindigo yields a monosulphonic acid readily soluble in water or alcohol; its solutions have a purple-red colour, but dye green; the alkali salts are obtained as flocculent precipitates when a solution of the acid is poured into solutions of sodium or potassium chloride. The *β*-disulphonic acid is formed when the indigo is left in contact with fuming sulphuric acid containing 25 per cent. of anhydride, and is best isolated in the form of its potassium salt, which crystallises in small needles; with the same acid, but at a higher temperature, a *trisulphonic acid* is obtained. A *tetrasulphonic acid* may be prepared by the aid of sulphuric acid containing 40 per cent. of anhydride or of chlorosulphonic acid. All the sulphonic acids dye wool a bluish-green colour; the tone is good, and the colours are very fast. J. J. S.

**Quinoline Perhaloids.** By PERRY F. TROWBRIDGE (*J. Amer. Chem. Soc.*, 1899, 21, 66—72).—*Quinoline hydriodide*,  $\text{C}_9\text{NH}_7\text{HI}$ , obtained by heating quinoline with a slight excess of hydriodic acid, forms yellow, acicular crystals which dissolve in alcohol, and melts at 135°.

*Quinoline methobromide*,  $\text{C}_9\text{NH}_7\text{MeBr}$ , prepared by passing methylic bromide into quinoline, crystallises in colourless needles melting at

70°; it is readily soluble in water, alcohol, ether, or chloroform, slightly so in acetone, and almost insoluble in light petroleum or benzene.

*Quinoline hydrobromide tetrabromide*,  $C_9NH_7.HBr.Br_4$ , obtained on adding a slight excess of hydrobromic acid to quinoline and saturating the mixture with bromine vapour, forms dark red, cubic crystals which melt at 39°, and on exposure to the air give off bromine, the residue consisting of a mixture of lower perbromides melting at 88°.

*Quinoline hydrobromide dibromide*,  $C_9NH_7.HBr.Br_2$ , obtained by saturating an aqueous solution of quinoline hydrochloride with bromine, forms fine, red crystals melting at 98–99°.

*Quinoline methobromide dibromide*,  $C_9NH_7.CH_3Br.Br_2$ , obtained by saturating aqueous quinoline methobromide with bromine, separates in the form of a yellow precipitate, gradually changing to a heavy oil, which, on exposure to the air, is converted into a crystalline mass; it is almost insoluble in water or ether, but dissolves slightly in chloroform, and more so in alcohol, from which it crystallises in yellow needles melting at 108°.

*Quinoline hydriodide tetriodide*,  $C_9NH_7.HI.I_4$ , gradually separates from a mixture of alcoholic iodine with either the aqueous hydriodide or hydrobromide of quinoline; it crystallises in lustrous, black plates melting at 76°.

*Quinoline methiodide tetriodide*,  $C_9NH_7.CH_3I.I_4$ , obtained by adding an excess of alcoholic iodine to aqueous quinoline metho-chloride, -bromide, or -iodide, form greenish-black crystals melting at 70°.

*Quinoline hydrochloride bromide*,  $C_9NH_7.HCl.Br$ , prepared by passing chlorine into a solution of quinoline and hydrobromic acid in much water, crystallises in fine, yellow needles melting at 101–102°.

*Quinoline methochloride bromide*,  $C_9NH_7.CH_3Cl.Br$ , separates on saturating aqueous quinoline methobromide with chlorine; it crystallises in yellow scales melting at 112°.

*Quinoline hydrochloride iodochloride*,  $C_9NH_7.HCl.ICl$ , formed when a warm aqueous solution of quinoline hydriodide is saturated with chlorine, crystallises in long, yellow prisms melting at 112°.

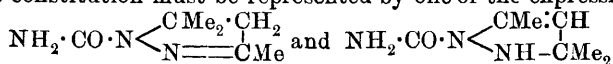
*Quinoline methochloride iodochloride*,  $C_9NH_7.CH_3Cl.ICl$ , prepared by saturating a warm, aqueous solution of quinoline methiodide with chlorine, forms fine, yellow crystals.

*Quinoline hydrobromide iodobromide*,  $C_9NH_7.HBr.IBr$ , obtained by saturating aqueous quinoline hydriodide with bromine, crystallises in red crystals melting at 109°.

*Quinoline methobromide iodobromide*,  $C_9NH_7.CH_3Br.IBr$ , prepared by saturating aqueous quinoline methiodide with bromine, crystallises in yellow plates melting at 108°.

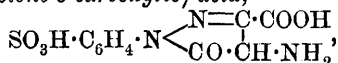
T. H. P.

**Behaviour of Mesitylic Oxide towards Semicarbazide.** By CARL D. HARRIES and FRIEDRICH KAISER (*Ber.*, 1899, 32, 1338–1339).—Scholtz has observed that the semicarbazone of mesitylic oxide, which melts at 156°, on distillation, yields an isomeride melting at 129° (*Abstr.*, 1896, i, 343); as this modification is not resolved into its components under the influence of acids, it is suggested that its constitution must be represented by one of the expressions



When mesitylic oxide is treated with an aqueous solution of semicarbazide hydrochloride in molecular proportion, it is dissolved in the course of 12 hours; if exactly neutralised with potassium carbonate, the solution yields the base derived from mesitylsemicarbazone on distillation. Whilst the semicarbazone melts and decomposes at 162—164°, the isomeric base melts at 130—131°; the latter also differs from the semicarbazone in forming a picrate, which crystallises in long, yellow prisms, and melts at 136—137°. M. O. F.

**Constitution of Tartrazine.** By RICHARD ANSCHÜTZ (*Annalen*, 1899, 306, 1—5. Compare Abstr., 1897, i, 258; also Gnehm and Benda, Abstr., 1898, i, 209).—*Aminotartrazinogenic* (1-*parasulphophenyl-4-amidopyrazolone-3-carboxylic*) acid,



obtained in association with sulphanilic acid by reducing tartrazine with zinc dust, crystallises from dilute hydrochloric acid in small needles; the solutions in alkali carbonates become violet on exposure to air, and concentrated sulphuric acid develops a dark violet coloration with the acid. The sodium salt forms colourless crystals which become reddish.

It is probable that aminotartrazinogenic acid is the parasulphonic derivative of diphenylizindihydroxytartaric acid, obtained by Tafel (Abstr., 1887, 467). M. O. F.

**Pyrimidine.** By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1899, 32, 1525—1538).—2-*Orthomethoxyphenyl-4-methylpyrimidone*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{N} \cdot \text{CMe} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH}$ , prepared by condensing anisamidine with ethylic acetoacetate under the influence of caustic soda, crystallises from dilute alcohol in aggregates of slender needles and melts at 202—203°; phosphorus oxychloride converts it into 2-*methoxyphenyl-4-methyl-6-chloropyrimidine*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{N} \cdot \text{CMe} \\ \text{N}=\text{CCl} \end{array} \text{CH}$ , which forms silky needles melting at 89—90°. 2-*Hydroxyphenyl-4-methylpyrimidone*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{N} \cdot \text{CMe} \\ \text{NH} \cdot \text{CO} \end{array} \text{CH}$ , obtained on reducing the chlorobase with hydriodic acid and phosphorus, forms small prisms and does not melt below 265°.

When acetylacetone is added to an ethereal solution of anisamidine, the additive compound,  $\text{C}_8\text{H}_{10}\text{N}_2 + \text{C}_5\text{H}_8\text{O}_2$ , separates in colourless leaflets (compare Pinner, Abstr., 1893, i, 735). 2-*Methoxyphenyl-4:6-dimethylpyrimidine*,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CMe} \end{array} \text{CH}$ , prepared by heating the additive compound at 140°, melts at 96—97°; it dissolves in dilute hydrochloric acid, and the solution yields crystalline compounds with platinum tetrachloride and with potassium dichromate. 2-*Hydroxyphenyl-4:6-dimethylpyrimidine*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CMe} \end{array} \text{CH}$ , obtained on hydrolysing the methylic ether with concentrated hydrobromic acid, crystallises from dilute alcohol in silky needles and melts at 178—179°.



4 : 6-Dimethylpyrimidine-2-carboxylic acid,  $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CMe} \end{smallmatrix} \text{CH}$ , prepared by oxidising hydroxyphenyldimethylpyrimidine with a 5 per cent. solution of potassium permanganate, crystallises from warm water in long, silky needles, which become opaque in air, owing to loss of water; it melts at  $145-146^\circ$ . 4 : 6-Dimethylpyrimidine,  $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CMe} \end{smallmatrix} \text{CH}$ , produced on submitting the carboxylic acid to dry distillation, melts at  $25^\circ$  and boils at  $159^\circ$  under 768 mm. pressure; it is miscible with water, forming a solution which is neutral towards litmus. The *platinochloride* forms orange-yellow, rhombic crystals, and melts at  $103-104^\circ$ ; the *picrate* is sparingly soluble, and crystallises in leaflets melting at  $142-143^\circ$ .

4-Methyl-2 : 6-dichloropyrimidine,  $\text{CCl} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CCl} \end{smallmatrix} \text{CH}$ , obtained by heating methyluracil with phosphorus oxychloride, crystallises from petroleum in colourless needles and melts at  $46-47^\circ$ ; the substance boils at  $219^\circ$ , and the vapour in steam has an irritating odour. Reduction with hydriodic acid and phosphorus converts it into hydroxymethylpyrimidine *hydriodide*,  $\text{OH} \cdot \text{C}_4\text{H}_2\text{MeN}_2\text{HI}$ , which crystallises in yellowish rhombohedra, sinters at  $150^\circ$ , and melts to a dark red liquid at  $185-187^\circ$ . Fuming hydriodic acid alone reduces the dichlorobase to methylodopyrimidine,  $\text{C}_4\text{H}_2\text{IMeN}_2$ , the *hydriodide* of which melts at  $112-114^\circ$  when rapidly heated; the *picrate* forms yellow rhombs, and melts at  $120-121^\circ$ .

4-Methylpyrimidine,  $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{N} = \text{CH} \end{smallmatrix} \text{CH}$ , prepared by reducing methylchloropyrimidine with zinc dust and water, boils at  $141.5-142^\circ$  under 762 mm. pressure, and has a sp. gr. 1.031 at  $16^\circ$ ; it is a mobile oil which mixes with water, and is indifferent towards litmus. The *aurichloride* melts at  $115^\circ$ , and the *mercurichloride* crystallises in slender needles melting at  $198^\circ$ ; the *picrate* forms rhombic leaflets, and melts at  $131-134^\circ$ . Pyrimidine-4-carboxylic acid,  $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{C}(\text{COOH}) \\ \text{N} = \text{CH} \end{smallmatrix} \text{CH}$ , obtained on oxidising a boiling solution of methylpyrimidine with 2 per cent. potassium permanganate, separates from water in colourless crystals and melts at  $240^\circ$ ; the *copper* salt crystallises in pale blue rhombs which become opaque at  $100^\circ$ .

Pyrimidine,  $\text{CH} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} \cdot \text{CH} \end{smallmatrix} \text{CH}$ , is formed from the carboxylic acid on distillation, and melts at  $20-22^\circ$ , boiling at  $123.5-124^\circ$  under 762 mm. pressure; it has a penetrating, stupefying odour, and mixes with water forming a solution neutral towards litmus. The *mercurichloride* and *aurichloride* crystallise in needles, the latter salt melting at  $226^\circ$ ; the *picrate* forms yellow, silky needles, and melts at  $156^\circ$ . M. O. F.

**Benzimidazoles.** By REINHOLD WALTHER and TH. VON PULAWSKI (*J. pr. Chem.*, 1899, [ii], 59, 249-265).—Dibenzorthophenylenediamide is somewhat sparingly soluble in hot acetic acid and is insoluble in acids, alkalis, benzene, ether, or water, and melts at  $300^\circ$  (compare *Abstr.*, 1891, 1130).

2'-Phenylbenzimidazole,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} \text{C} \cdot \text{Ph}$ , made by heating the preceding compound with hydrochloric acid in closed tubes at  $200^\circ$ , or by heating orthophenylenediamine with benzoic acid at  $180^\circ$ , crystallises in tablets, melts at  $280^\circ$  (compare Hübner, Abstr., 1881, 1131), is sparingly soluble in cold concentrated hydrochloric acid, but more readily in the hot liquid, yielding the hydrochloride.

*Diphenacetorthophenylenediamide*,  $C_6H_4(\text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Ph})_2$ , crystallises in beautiful, white needles, and melts at  $168^\circ$ ; it is somewhat readily soluble in hot benzene, alcohol, or acetic acid, and insoluble in alkalis, acids, water, or ether.

2'-Benzylbenzimidazole,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{Ph}$ , made by heating the preceding compound with hydrochloric acid at  $140^\circ$ , or, more simply, by heating orthophenylenediamine and phenylacetic acid at  $180^\circ$ , crystallises from benzene in well-formed, white needles, melts at  $187^\circ$ , and is very readily soluble in cold acetic acid, more sparingly in hot benzene, and insoluble in ether. The *hydrochloride*,  $C_{14}H_{13}N_2Cl$ , crystallises in beautiful tablets, the *nitrate*,  $C_{14}H_{13}N_3O_3$ , in beautiful, shining needles; both salts are hydrated and effloresce on exposure to air. The *sulphate*, *oxalate*, and *hydriodide* all crystallise well. The *platinochloride*,  $(C_{14}H_{12}N_2)_2 \cdot H_2PtCl_6$ , crystallises in small, yellow prisms. The *picrate*,  $C_{14}H_{12}N_2 \cdot C_6H_3N_3O_7$ , forms yellow leaflets and melts at  $214^\circ$ . When the base is heated in alcoholic solution with excess of iodine, it yields a *tri-iodide*,  $C_6H_4 \begin{smallmatrix} \text{NH}_2\text{I}_3 \\ \text{---} \text{N} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{Ph}$ , which crystallises from acetic acid in dark red prisms and decomposes, on prolonged heating with water, into the hydriodide of the base and free iodine.

*Phenylenedibenzimidazole*,  $C_6H_4 \left( C \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} C_6H_4 \right)_2$ , formed when orthophenylenediamine is heated with phthalic anhydride at  $180^\circ$ , is insoluble in the usual media, does not melt at  $310^\circ$ , and with mineral acids, yields well crystallised salts which dissociate in dilute solution partly into the monacid salt, and partly into free base. The *platinochloride*,  $C_{20}H_{14}N_4 \cdot H_2PtCl_6$ , is a yellow, microcrystalline powder; the *picrate* crystallises in yellow needles and melts at  $250^\circ$ .

*Ethylenedibenzimidazole*,  $C_2H_4 \left( C \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} C_6H_4 \right)_2$ , formed by heating orthophenylenediamine with succinic anhydride at  $180^\circ$ , is insoluble in the ordinary media, and forms a white, amorphous substance melting above  $310^\circ$ . The *hydrochloride*,  $C_{16}H_{14}N_4 \cdot 2HCl$ , forms beautiful, shining leaflets, the *platinochloride*,  $C_{16}H_{16}N_4Cl_6Pt$ , is a yellow, microcrystalline substance, and the *picrate*,  $C_{28}H_{20}N_{10}O_{14}$ , decomposes above  $270^\circ$ .

*Dimetanitrobenzophenylenediamide*,  $C_6H_4(\text{NH} \cdot \text{CO} \cdot C_6H_4 \cdot \text{NO}_2)_2$ , crystallises in beautiful, white needles, melts at  $240^\circ$ , and is somewhat readily soluble in hot acetic acid or alcohol, sparingly soluble in hot benzene, and insoluble in water, acids, or alkalis.

2'-Metanitrophenylbenzimidazole,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} \text{C} \cdot C_6H_4 \cdot \text{NO}_2$ , crystal-

lises from dilute alcohol in yellow needles melting at  $204^{\circ}$ , has feeble basic properties, and is scarcely soluble in mineral acids, dissolves readily in acetic acid or alcohol, and sparingly in benzene or water. The *picrate*,  $C_{19}H_{12}O_9N_6$ , forms yellow needles and melts at  $254^{\circ}$ .

*Diorthonitrobenzophenylenediamide*,  $C_6H_4(NH \cdot CO \cdot C_6H_4 \cdot NO_2)_2$ , crystallises in beautiful, pale yellow needles melting at  $265^{\circ}$ , and is soluble in warm acetic acid or alcohol, but insoluble in benzene, ether, acids, or alkalis.

*2'-Orthonitrophenylbenzimidazole*,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} > C \cdot C_6H_4 \cdot NO_2$ , crystallises from dilute alcohol in shining, brownish leaflets melting at  $263^{\circ}$ , and is very readily soluble in acetic acid or alcohol, sparingly so in hot benzene, and insoluble in water or ether. The *picrate* forms small needles and melts at  $200^{\circ}$ .

*Monoparanitrobenzophenylenediamide*,  $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$ , crystallises from boiling water in yellow needles, melts at  $240^{\circ}$ , and dissolves readily in cold acetic acid, alcohol, or hot benzene, but is only sparingly soluble in water. It yields the corresponding benzimidazole by continued boiling with strong hydrochloric acid.

*Diparanitrobenzophenylenediamide*,  $C_6H_4(NH \cdot CO \cdot C_6H_4 \cdot NO_2)_2$ , crystallises in beautiful, yellowish prisms, and is soluble in hot acetic acid or alcohol, but insoluble in water, acids, alkalis, benzene, or ether; when heated under pressure with strong hydrochloric acid, it yields the corresponding imidazole.

*α-Paranitrophenylbenzimidazole*,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} > C \cdot C_6H_4 \cdot NO_2$ , crystallises in yellowish-brown prisms, does not melt below  $310^{\circ}$ , and is readily soluble in cold acetic acid or alcohol, but insoluble in the other common media. It is identical with the substance obtained by Hinsberg and Funke by the action of paranitrobenzaldehyde on orthophenylenediamine. Its basic properties are very feeble, and it is scarcely soluble in strong hydrochloric acid. The *picrate*,  $C_{19}H_{12}N_6O_9$ , crystallises in yellow needles and decomposes at about  $250^{\circ}$ . A. L.

**Benzimidazolecarboxylic Acid.** By OTTO FISCHER (*Ber.*, 1899, 32, 1312—1315).—*αβ-Naphthimidazole*,  $CH \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} > C_{10}H_6$ , is best prepared by heating together a mixture of *αβ-naphthylenediamine*, formic acid, and sodium formate at  $130$ — $140^{\circ}$  for 10 hours; the *aurichloride* forms orange-red needles which melt at  $269^{\circ}$ , and the *platinochloride* separates from hot water in small, yellow needles. The *tetrahydro*-compound,  $C_{11}H_{12}N_2$ , obtained on reduction with sodium and amyllic alcohol, forms slender, white needles melting at  $196^{\circ}$ ; the *aurichloride* forms small, yellow needles, and the *platinochloride* orange-red needles.

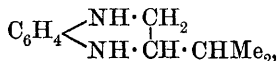
*Benzimidazole-1 : 2-dicarboxylic acid*,  $CH \begin{smallmatrix} \text{NH} \\ \text{---} \text{N} \end{smallmatrix} > C_6H_2(COOH)_2$ , is obtained by the oxidation of naphthimidazole with chromic anhydride, and crystallises from hot water in white, glistening leaflets melting at  $251^{\circ}$ , it is readily soluble in alcohol, glacial acetic acid, or hot water, sparingly so in ether or light petroleum; the *silver* salt is a white, flocculent precipitate, and has the formula  $C_9H_4N_2O_4Ag_2$ , so

that the acid is dibasic, but as on titration only 1 mol. of normal potassium hydroxide is required, it is evident that one of the carboxyl groups is neutralised by the imido-group. On heating at 150°, the acid gradually passes into its *anhydride*,  $C_9H_4N_2O_3$ , which melts at 224—225° and sublimes in needles. On boiling the acid with aniline, a compound corresponding with phthalanil is formed, which crystallises from hot alcohol in needles. With phenols, the acid and its anhydride behave in the same way as phthalic acid and phthalic anhydride, forming products similar to phenolphthalein and fluorescein. The *dimethylic* salt crystallises from alcohol in white needles which soften at 231°; the fact that, on boiling this ethereal salt with dilute hydrochloric acid, the original acid is regenerated, shows that the substance is a true dimethylic salt and does not contain a methyl group attached to the imido-nitrogen.

J. F. T.

**Action of Orthophenylenediamine on Ethylic Bromodimethylacetoacetate.** By MAX CONRAD and KARL HOCK (*Ber.*,

1899, 32, 1208—1210).—2'-*Isopropylquinoxaline*,  $C_6H_4 \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} \cdot \text{C} \cdot \text{CHMe}_2 \end{smallmatrix}$ , formed by the action of orthophenylenediamine on ethylic bromodimethylacetoacetate in alcoholic solution, is a colourless oil, which boils at 269—270°, has a sharp taste, and smells of peppermint. On reduction, it yields *isopropyltetrahydroquinoxaline*,



which melts at 75°, can be distilled without undergoing decomposition, and gives the characteristic blue coloration with ferric chloride.

A. H.

**Quinazoline Derivatives.** By ALEXANDER DRAWERT (*Ber.*, 1899, 32, 1259—1266. Compare Gabriel and Stelzner, *Abstr.*, 1896, i, 506).—Metaxylenephthalic acid (*Abstr.*, 1882, 848) is converted into the chloride by dissolution in warm benzene and treatment with phosphorus pentachloride; the solution is then well cooled, saturated with ammonia, mixed with slightly ammoniacal water, and the benzene removed by distillation with steam; the residue on cooling yields a brown deposit of *metaxylenephthalamide*,  $C_6H_3Me_2 \cdot CO \cdot C_6H_4 \cdot CO \cdot NH_2$ , which, on crystallisation from toluene, forms slightly brown plates melting at 152—153°.

2:4-*Dimethylorthamidobenzophenone*,  $C_6H_3Me_2 \cdot CO \cdot C_6H_4 \cdot NH_2$ , is prepared by mixing the moist and very finely divided amide with 10 per cent. sodium hydroxide and treating with sodium hypobromite, the mixture being well stirred and cooled; it crystallises in yellow plates, melts at 89°, and is readily soluble in the usual solvents; the *hydrochloride*,  $C_{15}H_{15}NO, HCl$ , forms colourless, compact crystals melting and decomposing at 170°; it gradually loses hydrogen chloride when kept; the *picrate* crystallises in small, yellow needles melting at 100—101°, and the *benzoyl* derivative in needles melting at 124°.

4-*Xylylquinazolone*,  $C_6H_4 \begin{smallmatrix} \text{C}(C_8H_9) \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{N}$ , obtained when the amido-ketone is heated with carbamide, first at 175°, and finally at 195°, forms colourless needles melting at 260—261°; it has neither odour

nor taste, and is readily soluble in dilute acids or alkalis. The *hydrochloride*,  $C_{16}H_{14}N_2O \cdot HCl$ , forms small, reddish-yellow needles, and the *sulphate*,  $(C_{16}H_{14}N_2O)_2 \cdot H_2SO_4$ , orange-yellow needles melting and decomposing at  $261^\circ$ ; the *dichromate* turns brown at  $150^\circ$  and blackens at  $165^\circ$ ; the *picrate* crystallises in yellow needles, sinters at  $210^\circ$ , and melts at  $214^\circ$ .

2-Chloro-4-xylylquinazoline,  $C_6H_4 \langle \begin{smallmatrix} C(C_8H_9) \\ N=CCl \end{smallmatrix} \rangle N$ , is obtained when the quinazolone is boiled for half an hour with phosphorus pentachloride and oxychloride; it crystallises from ether in colourless needles melting at  $126^\circ$ , and is partially re-converted into the quinazolone by recrystallisation from boiling alcohol. The orthamidoketone is readily reduced by sodium amalgam (2.5 per cent.) and aqueous alcohol, yielding 2:4-dimethylorthamidobenzhydrol,  $NH_2 \cdot C_6H_4 \cdot CH(OH) \cdot C_6H_3Me_2$ , which crystallises in colourless prisms melting at  $103^\circ$ , is readily soluble in most organic solvents, but sparingly in concentrated hydrochloric acid; salts could not be obtained; its *acetyl* derivative forms colourless needles melting at  $165^\circ$ . The amidobenzhydrol condenses with carbamide, yielding 4-xylyltetrahydro-2-ketoquinazoline,  $C_6H_4 \langle \begin{smallmatrix} CH(C_8H_9) \\ NH-CO \end{smallmatrix} \rangle NH$ , which crystallises from alcohol in colourless prisms melting at  $200^\circ$ , and yields an unstable *hydrochloride* crystallising in needles; the *acetate*,  $C_{16}H_{16}N_2O \cdot C_2H_4O_2$ , crystallises in colourless needles melting at  $118-119^\circ$ ; the *picrate* crystallises in yellow needles melting at  $160^\circ$ . 4-Xylyltetrahydro-2-thioquinazoline,  $C_6H_4 \langle \begin{smallmatrix} CH(C_8H_9) \\ NH-CS \end{smallmatrix} \rangle NH$ , obtained by the action of thiocyanic acid on the amidobenzhydrol, crystallises in needles or rhombic plates, which sinter at  $218^\circ$  and melt at  $222-223^\circ$ ; when an aqueous acetic acid solution is treated in the cold with bromine, 4-xylyldihydro-2-bromoquinazoline hydrobromide,  $C_6H_4 \langle \begin{smallmatrix} CH(C_8H_9) \\ N=CBR \end{smallmatrix} \rangle NH \cdot HBr$ , is obtained in the form of yellow, rhombic plates. The *base* separates from alcohol in crystals melting at  $170-171^\circ$ ; the *hydrobromide* turns brown at  $161^\circ$ , melts and decomposes at  $232-233^\circ$ , is insoluble in acetic acid, and only sparingly soluble in absolute alcohol; when boiled with aqueous alcohol, saturated with soda, and again boiled, it yields the ketoquinazoline.

J. J. S.

**New Types of Anhydro-compounds.** BY STEFAN VON NIEMENTOWSKI [and in part with St. KOZAKOWSKI] (*Ber.*, 1899, 32, 1456-1493. Compare *Abstr.*, i, 571, 1898, i, 210 and 337).—Acyl derivatives of  $\beta$ -orthamidobenzimidazoles are readily obtained when the compounds are heated with acids or acid anhydrides; they are characterised by the readiness with which they lose water and pass over into dianhydrides of the type  $\begin{smallmatrix} N \\ C_6H_4 \cdot N \end{smallmatrix} \begin{smallmatrix} =C \cdot C_6H_4 \\ =CR \end{smallmatrix} N$ . These anhydrides are usually obtained as bye-products during the preparation of the acyl derivatives, from which they may be separated by fractional crystallisation, and as a rule they are most readily obtained by

subjecting the crude acyl compounds to dry distillation. They stand in the same relationship to  $\beta$ -orthamidophenylbenzimidazole as does Hobercker's ethylenetolylenediamine to metaparatolylenediamine. Most of the anhydro-derivatives are reconverted into the acyl derivatives by rupture of the ring when boiled with alkalis or mineral acids.

*Orthonitrobenzorthonitranilide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , obtained by the action of orthonitrobenzoic chloride on orthonitriline, crystallises from acetic acid in pale yellow needles melting at  $167-168^\circ$ , is sparingly soluble in the usual solvents, most readily in acetone or acetic acid, dissolves readily in cold alkalis, and is only slowly hydrolysed when heated with concentrated hydrochloric acid at  $120^\circ$ . When exposed to sunlight, it changes colour and melts at a lower temperature; from this altered product, a small quantity of a substance melting at  $133-136^\circ$  has been isolated.

When the dinitranilide is reduced with zinc dust and 50 per cent. acetic acid, or with tin and hydrochloric acid in alcoholic solution, the only product is the corresponding diamido-derivative, but with tin and concentrated hydrochloric acid, stannous chloride and hydrochloric acid, or zinc dust and hydrochloric acid in alcoholic solution, the product is a mixture of the diamidoanilide and of  $\beta$ -orthamidophenylbenzimidazole; these may be extracted from the strongly alkaline liquid and separated by fractional crystallisation from alcohol. *Orthamidobenzorthamid-anilide* forms long, snow-white needles melting at  $129-130^\circ$ ; it is readily soluble in most organic solvents, somewhat sparingly, however, in light petroleum or in ether, but readily in most acids. When submitted to dry distillation, it loses water and yields  $\beta$ -orthamidophenylbenzimidazole (*loc. cit.*). Its *hydrochloride*,  $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2\text{HCl} + 2\text{H}_2\text{O}$ , forms slender needles which, when kept in the mother liquor, become gradually transformed into thick, compact crystals. When heated, it loses water, and finally becomes transformed into the hydrochloride of orthamidophenylbenzimidazole. The *platinochloride*,  $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2\text{H}_2\text{PtCl}_6$ , forms yellow prisms which do not melt at  $330^\circ$ .

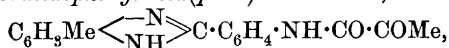
The *silver* derivative of  $\beta$ -orthamidophenylbenzimidazole has been obtained as a white precipitate insoluble in alcohol. *Orthonitrobenzo-metanitroparatoluidide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , crystallises in pale yellow prisms melting at  $198^\circ$ ; it is very sparingly soluble in alcohol, more readily in acetone, toluene, or acetic acid, and very readily in alkalis, yielding yellow solutions. When reduced with tin and hydrochloric acid, it yields a mixture of  $\beta$ -orthamidophenylmeta-(para)tolimidazole (*loc. cit.*), orthamidobenzometamidoparatoluidide, and  $\beta$ -orthamidophenylmeta-(para)oxytolimidazole, which may be separated by fractional crystallisation from alcohol. *Orthamidobenzometamidoparatoluidide* crystallises from alcohol in colourless rhomboidal plates melting at  $137^\circ$ ; at higher temperatures, it loses water and is converted into the corresponding tolimidazole melting at  $189^\circ$ ; it is readily soluble in chloroform or acetone, moderately in warm alcohol or benzene, and sparingly in ether, light petroleum, or water. When heated for several hours at  $180^\circ$  with concentrated hydrochloric acid, it is mainly converted into the tolimidazole, but part is decomposed into metaparatolylenediamine, aniline, and carbonic anhydride.

*β-Orthamidophenylmeta(para)oxylimidazole* is formed in small quantities (about 10 per cent.) ; it crystallises in colourless, compact crystals melting at 240°, dissolves readily in chloroform, alcohol, or acetone, but is only sparingly soluble in water, ether, or benzene, and is insoluble in alkalis.

*β-Orthacetamidophenylbenzimidazole*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$ , crystallises in needles melting and decomposing at 213—214°. *β-Orthacetamidoparatolylbenzimidazole*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NHAc}$ , may be readily separated from the anhydro-compound, which is formed at the same time, by its slight solubility in alcohol ; it crystallises in very slender needles melting at 252° and decomposing at 255°, is sparingly soluble in all organic solvents with the exception of hot acetic acid, dissolves readily in dilute acids and is not decomposed when boiled with alkalis.

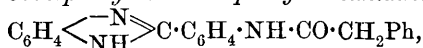
*Orthacetamidophenylmeta(para)tolimidazole*, obtained by heating orthamidobenzometamidoparatoluidide with acetic anhydride and distilling the product, crystallises from toluene in yellow, fibro-crystalline masses softening at 187° and melting at 193°.

*β-Orthopyruvamidophenylmeta(para)tolimidazole*,



obtained by heating together pyruvic acid and amidophenyltolimidazole, crystallises in intensely yellow needles containing 2H<sub>2</sub>O, which it loses at 105° ; it melts and decomposes at 254°, is sparingly soluble in most organic solvents, but dissolves readily in ammonia and also in hot mineral acids. When heated with phenylhydrazine, it yields pyruvic acid phenylhydrazone and orthamidophenyltolimidazole (m. p. 189°).

*β-Orthobenzamidophenylbenzimidazole*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NHBz}$ , crystallises from alcohol in long, colourless needles melting at 251°. *β-Benzamidoparatolylbenzimidazole* crystallises from alcohol in needles melting at 268°, is very sparingly soluble in most organic solvents, insoluble in ammonia, and only sparingly soluble in concentrated hydrochloric acid. *β-Orthophenylacetamidophenylbenzimidazole*,



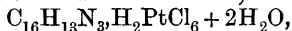
is obtained when the corresponding anhydro-compound is treated with benzoic chloride and alkali ; it crystallises from alcohol in slender needles melting at 240° and is readily soluble in most organic solvents.

*Methenyl-β-orthamidophenylbenzimidazole*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{N} = \text{CH}$ , crystallises in needles or plates melting at 227°, is very sparingly soluble in ether, readily in alcohol, benzene, or toluene, and very readily in chloroform or acetone ; it is insoluble in alkalis or ammonia, but dissolves in acids. When reduced with sodium and amyl alcohol, no definite product could be obtained, but on oxidation with chromic anhydride, carbonyl-β-orthamidophenylbenzimidazole is formed. When oxidised with alkaline permanganate, the same product is

obtained together with a scarlet substance melting at 300°. Benzoic chloride and alkali are without action on the methenyl compound; mineral acids hydrolyse it so readily that definite salts cannot be obtained.

*Ethenyl-β-orthamidophenylbenzimidazole*,  $\begin{array}{c} \text{N}=\text{C}\cdot\text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CMe} \end{array} \gg \text{N}$ , crystallises in prisms melting at 177–178°; its *hydrochloride* forms minute needles melting at 252°, and when treated with sodium nitrite yields the azimide of β-orthamidophenylbenzimidazole (*loc. cit.*). When the ethylene base is reduced with sodium and amyl alcohol, β-orthamidophenylbenzimidazole is formed. *Propenyl-β-orthamidophenylbenzimidazole* forms hard, compact crystals melting at 147°, and is readily soluble in hot ether, benzene, alcohol, &c. Its *hydrochloride* crystallises with  $\frac{1}{2}\text{H}_2\text{O}$ , and yields two *platinochlorides*, namely,  $(\text{C}_{16}\text{H}_{13}\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$  and  $\text{C}_{16}\text{H}_{13}\text{N}_3\cdot\text{H}_2\text{PtCl}_6 + 1\frac{1}{2}\text{H}_2\text{O}$ . When oxidised with chromic anhydride, it gives a theoretical yield of carbonyl-β-orthamidophenylbenzimidazole. *Benzenyl-β-orthamidophenylbenzimidazole* crystallises in long, silky needles melting at 239°, and is readily soluble in cold chloroform; the *hydrochloride*,  $\text{C}_{20}\text{H}_{13}\text{N}_3\cdot\text{HCl}$ , crystallises in small plates melting and decomposing at 235°. *Phenyl-*

*ethenyl-β-orthamidophenylbenzimidazole*,  $\begin{array}{c} \text{N}=\text{C}—\text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}(\text{CH}_2\text{Ph}) \end{array} \gg \text{N}$ , obtained by heating a mixture of phenylacetic acid and β-orthamidophenylbenzimidazole moistened with ethylic phenylacetate, crystallises in needles melting at 196°, and when oxidised with chromic anhydride, yields benzoic acid and carbonylamidophenylbenzimidazole. *Methenyl-β-orthamidoparatolylbenzimidazole* crystallises in feathery needles, softens at 200°, and melts at 215°; the *hydrochloride* and *sulphate* are readily soluble in water; the *platinochloride*,  $\text{C}_{15}\text{H}_{11}\text{N}_3\cdot\text{H}_2\text{PtCl}_6 + 3\text{H}_2\text{O}$ , darkens at 250°, but does not melt at 300°. During the preparation of the methenyl base, a bye-product, probably β-orthoformamidoparatolylbenzimidazole, is obtained, which dissolves in acids, yielding a pale green, fluorescent solution. *Ethenyl-β-orthamidoparatolylbenzimidazole* crystallises in needles, prisms, or plates melting at 187–189°; its salts are readily soluble in water or alcohol; the *platinochloride*,



forms pale yellow needles, and the *aurichloride* golden-yellow plates melting at 225°. The action of bromine on this base has been studied, but the products have not been examined in detail. *Benzenyl-β-orthamidoparatolylbenzimidazole* crystallises in snow-white, glistening needles melting at 240–241°; the *platinochloride*,  $(\text{C}_{21}\text{H}_{15}\text{N}_3)_2\cdot\text{H}_2\text{PtCl}_6$ , forms straw-coloured crystals melting and decomposing at 286°.

*Methenyl-β-orthamidophenylmeta(para)tolimidazole* crystallises in groups of concentric needles melting at 237° and is only sparingly soluble in ether; when heated with concentrated hydrochloric acid in sealed tubes, it is hydrolysed to β-orthamidophenylmeta(para)tolimidazole *hydrochloride* melting and decomposing at 245°. *Ethenyl-β-orthamidophenylmeta(para)tolimidazole acetate* crystallises in needles which soften at 135° and melt at 142°; when heated at 105°, it loses acetic acid and yields the base,  $\text{C}_{16}\text{H}_{13}\text{N}_3$ , which crystallises, with  $2\text{H}_2\text{O}$ , in long needles melting at 160°. *Methenyl-β-orthamidoparatolylmeta(para)tolimidazole*



crystallises in needles melting at  $212^{\circ}$ , and on oxidation yields the corresponding carbonyl compound. *Ethenyl- $\beta$ -orthamidoparatolyl-meta(para)tolimidazole* has not been obtained in a pure form; different fractions melting at  $218^{\circ}$ ,  $193^{\circ}$ , and  $172^{\circ}$  gave practically the same results on analysis.

*Carbonyl- $\beta$ -orthamidophenylbenzimidazole*,  $\begin{array}{c} \text{N}=\text{C}\cdot\text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4\cdot\text{N}-\text{CO} \end{array} > \text{NH}$ , may be obtained either by the oxidation of the corresponding methylene compound with chromic anhydride, or, still better, by the condensation of  $\beta$ -orthamidophenylbenzimidazole (1 part) with carbamide (2—3 parts); it crystallises from acetic acid with 1 mol. of acid, which it loses at  $104^{\circ}$  and then melts at  $334^{\circ}$ , is sparingly soluble in most solvents, and has feebly basic and also acid properties. It is more stable than the methylene derivative, and is only hydrolysed when heated at  $190^{\circ}$  with concentrated hydrochloric acid; two *hydrochlorides*,  $\text{C}_{14}\text{H}_9\text{N}_3\text{O}\cdot\text{HCl}$  and  $\text{C}_{14}\text{H}_9\text{N}_3\text{O}\cdot 2\text{HCl}$ , exist, but both are unstable, and give up all their acid at  $105^{\circ}$ . The *sulphate* forms colourless needles melting at  $298^{\circ}$ . When treated with nitric acid of sp. gr. 1.52, the carbonyl compound yields a *dinitro-derivative*,  $\text{C}_{14}\text{H}_7\text{N}_5\text{O}_5$ , which crystallises in minute needles melting at  $315^{\circ}$ ; it is sparingly soluble in most solvents, and has a more pronounced acid character than the original substance. *Carbonyl- $\beta$ -orthamidophenylmeta(para)tolimidazole*,  $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}$ , obtained by the action of carbonyl chloride on the amidophenyl-tolimidazole, crystallises in snow-white needles or glistening plates melting at  $343^{\circ}$ . *Carbonyl- $\beta$ -orthamidoparatolylmeta(para)tolimidazole*,  $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}$ , forms small, crystalline aggregates melting at  $182^{\circ}$ ; it differs from the other carbonyl derivatives in being readily soluble in most organic solvents.

*Thiocarbonyl- $\beta$ -orthamidophenylbenzimidazole*,  $\text{C}_{14}\text{H}_9\text{N}_3\text{S}$ , obtained by heating amidophenylbenzimidazole with carbon bisulphide, first at  $155^{\circ}$  and then at  $185^{\circ}$ , crystallises in pale yellow needles melting at  $291^{\circ}$ ; it is readily soluble in hot chloroform, acetone, or acetic acid, also in alkalis, but only sparingly in alcohol or benzene; it is very stable, and is not hydrolysed when heated at  $170^{\circ}$  with concentrated hydrochloric acid. When orthamidophenylbenzylimidazole is condensed with glycerol, nitrobenzene, and sulphuric acid by Skraup's method,  *$\beta$ -orthoquinolinebenzimidazole*,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N} \\ \text{NH} \end{array} > \text{C}\cdot\text{C}_9\text{NH}_6$ , is obtained, the yield being about 50 per cent. of the theoretical; it crystallises in concentrically arranged, brownish-yellow needles containing  $1\text{H}_2\text{O}$ , which it loses at  $105^{\circ}$ , melts at  $124^{\circ}$ , and is readily soluble in most organic solvents; the *sulphate*,  $\text{C}_{16}\text{H}_{11}\text{N}_3\cdot\text{H}_2\text{SO}_4$ , crystallises in yellowish, nodular masses melting at  $287^{\circ}$ . J. J. S.

**Some Amido- $\alpha$ -phenylbenzoxazole Derivatives.** By OTTO KYM (*Ber.*, 1899, 32, 1427—1432. Compare Pinnow and Wiskott, this vol., i, 500).—Dinitrophenylic benzoate is obtained in quantitative yield by heating 2:4-dinitrophenol with benzoic chloride for 2 hours at  $180$ — $200^{\circ}$ . By reducing it cautiously with stannous chloride and hydrochloric acid, yellow  *$\alpha$ -phenylmetamidobenzoxazole*,

$\text{NH}_2 \cdot \text{C}_6\text{H}_3 \langle \text{O} \rangle_{\text{N}} \text{CPh}$ , melting at  $151-152^\circ$  is obtained. This reacts with acetic anhydride at the ordinary temperature, forming an *acetyl* derivative, which melts at  $181-182^\circ$ .

Trinitrophenylic benzoate, from picric acid and benzoic chloride, when cautiously reduced with stannous chloride, or tin and hydrochloric acid (Nietzki, Abstr., 1897, i, 277), yields a very little of the yellowish-green  $\alpha$ -phenylmetadiamidobenzoxazole,  $\text{C}_6\text{H}_2(\text{NH}_2)_2 \langle \text{O} \rangle_{\text{N}} \text{CPh}$ , melting at  $203-204^\circ$ , the *diacetyl* derivative of which melts at  $277-278^\circ$ . This substance is better prepared by reducing, according to Nietzki's method,  $\alpha$ -phenylmetadinitrobenzoxazole, which melts at  $224-225^\circ$  (not  $218^\circ$ ), and is prepared by heating picramic acid with benzoic chloride and boiling the benzoylpicramic acid so obtained (which melts at  $229-230^\circ$ , not  $220^\circ$ ) with acetic anhydride, or by boiling picramic acid with benzoic chloride in nitrobenzene solution.

Dinitrophenylic paranitrobenzoate, from 2:4-dinitrophenol and paranitrobenzoic chloride, melts at  $139-140^\circ$ , and when reduced with stannous chloride and hydrochloric acid, yields *paramido- $\alpha$ -phenylmetamidobenzoxazole*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \langle \text{O} \rangle_{\text{N}} \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , which melts at  $229-230^\circ$ , and forms a *diacetyl* derivative melting at  $278-279^\circ$ .

C. F. B.

**Reaction of Alkaloids with Ortho-xylylenic Bromide.** By MAX SCHOLTZ (*Arch. Pharm.*, 1899, 237, 200-211).—The alkaloid was heated with ortho-xylylenic bromide in alcoholic, or occasionally chloroform, solution on the water-bath, and the whole then set aside. From the bromide so obtained, a chloride was prepared by treatment with silver chloride, or with silver oxide and water, and hydrochloric acid successively. The alkaloids react like the aliphatic amines (Abstr., 1898, i, 565). If they are tertiary bases,  $\text{NR}'''$ , they yield di- or mon-ammonium bromides,  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{NR}''' \text{Br})_2$  or  $\text{CH}_2 \text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NR}''' \text{Br}$ , according to the proportions which are taken. If they are di-acid bases, a number of products are possible, and several of them seem to be formed in the case of quinine, although none could be isolated; in the case of nicotine, the two compounds,  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2\text{Br})_2$  and  $\text{C}_6\text{H}_4 \langle \text{CH}_2 \rangle_{\text{CH}_2} \text{C}_{10}\text{H}_{14}\text{N}_2\text{Br}_2$ , were actually obtained pure. In the case of the secondary base coniine, the compound  $\text{C}_6\text{H}_4 \langle \text{CH}_2 \rangle_{\text{CH}_2} \text{NBr} \langle \text{CHPr} \cdot \text{CH}_2 \rangle_{\text{CH}_2 - \text{CH}_2} \text{CH}_2$ , is formed (1 mol. of caustic potash is added to neutralise the hydrogen bromide formed simultaneously). This compound, when heated with ammonia at  $200^\circ$ , yields a diamine,  $\text{C}_6\text{H}_4 \langle \text{CH}_2 \cdot \text{NH} \cdot \text{CHPr} \cdot \text{CH}_2 \rangle_{\text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 - \text{CH}_2} \text{CH}_2$ , which forms a nitroso-derivative, both  $\text{NH}$ -groups in which are converted into  $\text{N} \cdot \text{SO}_2\text{Ph}$ -groups when the diamine is suspended in dilute caustic potash and shaken with benzenesulphonic chloride.

The compounds obtained are enumerated below with their melting points under the names of the alkaloids from which they were prepared. From atropine:  $\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{C}_{17}\text{H}_{23}\text{NO}_3\text{Br})_2$ ,  $145^\circ$ ; *aurichloride*,  $78^\circ$ ;

*platinochloride*, 240—241°. From tropine:  $C_6H_4(CH_2 \cdot C_8H_{15}NOBr)_2$ , 230—231°; *platinochloride*, 246—247°; *aureichloride*, 228—229°;  $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot C_8H_{15}NOCl$ , 160°; *platinochloride*, 196°; *aureichloride*, 62°. From strychnine:  $C_6H_4(CH_2 \cdot C_{21}H_{22}N_2O_2Br)_2$ , 268—270°;  $CH_2Br \cdot C_6H_4 \cdot CH_2 \cdot C_{21}H_{22}N_2O_2Br$ , 200—203°. From brucine:  $C_6H_4(CH_2 \cdot C_{23}H_{26}N_2O_4Br)_2$ , 228—229°; *platinochloride*. From narcotine:  $C_6H_4(CH_2 \cdot C_{22}H_{25}NO_7Br)_2$ , 160—162°. From papaverine:  $C_6H_4(CH_2 \cdot C_{20}H_{21}NO_4Br)_2$ , 207—208°, gives a yellow precipitate with caustic soda. From nicotine:  $C_6H_4(CH_2 \cdot C_{10}H_{14}N_2Br)_2$ , 95—97°;  $C_6H_4 \cdot C_2H_4 \cdot C_{10}H_{14}N_2Br_2$ , 158—159°; *platinochloride*, *aureichloride*. From coniine: *ammonium bromide* (see above); *platinochloride*, 193°; *diamine* boils at 215—218° under 25 mm. pressure; *dibenzenesulphonamide*, 117°. C. F. B.

**Derivatives of Morphine.** By EMMANUEL MERCK (*Arch. Pharm.*, 1899, 237, 211—222).—The *hydrochlorides* of *propylic*, *isobutylic*, and *amylic morphine carbonates*,  $OH \cdot C_{17}H_{17}NO \cdot O \cdot COOR, HCl$ , were prepared by Otto and Holst's method (*Abstr.*, 1892, 638). The *platinochloride* of the *propylic* salt crystallises with  $2H_2O$ . In a similar manner, the *acetyl* derivative of the *ethyl* salt can be obtained from  $\alpha$ -acetylmorphine; it melts at about 150°; the *hydrochloride* melts and decomposes at 185°, the *platinochloride* at 210°; the latter crystallises with  $1H_2O$ .

The *hydrochloride* of *benzoylmorphine* (Sonntag, *Diss. Erlangen*, 1895), prepared by means of benzoic chloride, is actually precipitated from a solution containing excess of ammonia; it melts and decomposes at 176—177°; the base itself melts at 145°. *Dibenzoylmorphine* (Dankwort, *Abstr.*, 1891, 332), prepared by melting morphine with benzoic anhydride, forms a *hydrochloride*,  $C_{31}H_{27}NO_5, HCl + H_2O$ .

*Dimorphine ethylenic ether*,  $C_2H_4(C_{17}H_{18}NO_3)_2$ , is obtained by boiling morphine with alcoholic potash and ethylenic bromide; it melts at 188°. *Morphine benzylic ether*,  $C_{17}H_{18}NO_2 \cdot O \cdot CH_2Ph$ , is prepared by heating morphine with sodium ethoxide and benzylic chloride in alcoholic solution; both the base and its *hydrochloride*, "*peronine*," were prepared, but no analyses are given. Morphine ethylic ether,  $OH \cdot C_{17}H_{17}NO \cdot OEt + H_2O$ , melts at 93°, not 83°. Its *hydrochloride*, "*dionine*," melts and decomposes at 123—125°, and dissolves in 7 parts of water at the ordinary temperature. It will prove useful in therapeutics, as it is more soluble than any other derivative of morphine, except codeine phosphate, which has an acid reaction, and therefore causes pain when injected. C. F. B.

**Non-Nitrogenous Decomposition Products of Morphine.** V. By EDUARD VONGERICHTEN (*Ber.*, 1899, 32, 1521—1524. Compare this vol., i, 307).—*Diacetylmorpholquinone*,  $C_{18}H_{12}O_6$ , obtained from diacetylmorphol by the method employed for preparing acetylmethylmorpholquinone from acetylmethylmorphol, crystallises in yellow needles and melts at 196°; a brownish-red coloration is developed on dissolving the substance in concentrated sulphuric acid. The *azine* produced when the quinone undergoes condensation with orthotolylene-diamine, crystallises in yellowish needles and melts at 215—218°; the solution in concentrated sulphuric acid is deep blue, becoming red

when diluted with water. When diacetylmorpholquinone is treated with sodium methoxide dissolved in methylic alcohol, a cherry-red solution is first formed, and quickly becomes deep blue; addition of dilute mineral acid precipitates dihydroxyphenanthraquinone, which differs from the methylic ether in that it dyes fibre with a mordant.

The author gives reasons for representing the constitution of morphol by the formula  $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_4 \\ | \\ \text{CH} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \end{array}$  [CH:OH:OH=2:3:4], and that of morphenol by the second expression in the last communication on the subject (*loc. cit.*). M. O. F.

**Heroine [Diacetoxymorphine].** By G. WESENBERG (*Chem. Centr.*, 1899, i, 123; from *Pharm. Zeit.*, 1898, 43, 858).—*Diacetoxymorphine (heroine)*,  $\text{C}_{17}\text{H}_{17}\text{NO}(\text{OAc})_2$ , is a white, crystalline, odourless powder, has an alkaline reaction, melts at  $173^\circ$ , is almost insoluble in water, slightly soluble in cold alcohol and ether, and easily in chloroform, benzene, hot alcohol, and acids. The normal salts are hygroscopic and difficult to crystallise, whilst the acid salts, like the acid oxalate, generally crystallise well. The ordinary alkaloidal reagents form precipitates with solutions of the normal salts, a solution of iodine in potassium iodide giving a distinct turbidity with a solution containing only one part in 100,000. The colour reactions of morphine are also shown by diacetoxymorphine, but the blue coloration with potassium ferricyanide and ferric chloride is only formed after some time and nitric acid gives a yellow coloration. When treated with iodic acid, the diacetoxymorphine, unlike morphine, does not liberate iodine, and when digested with pepsin-hydrochloric acid containing 0.2 per cent. of acid, about a fourth part is decomposed into morphine and acetic acid. E. W. W.

**Alkaloids from Anhalonium Lewinii.** By E. KAUDER (*Arch. Pharm.*, 1899, 237, 190—198. Compare Heffter, *Abstr.*, 1895, i, 120; 1896, i, 267; 1898, i, 499).—Mezcal buttons, the dried heads of a Mexican cactus, *Anhalonium Lewinii* (or possibly *A. Williamsi*, as the two species can hardly be distinguished), were extracted with alcohol, the extract was freed from fat, and shaken with ammonia and chloroform, when a resin separated. The chloroform solution was shaken with water containing sulphuric acid, and the alkaloids so removed were separated into two groups, those of the first being readily soluble in ether, those of the second only slightly soluble in ether, but readily in chloroform. The alkaloids of the first group were separated by crystallisation of their hydrochlorides from absolute alcohol; anhalonine separated first, then pelletine, and finally lophophorine. The alkaloids of the second group were converted into sulphates and these crystallised from water; mezcaline sulphate crystallised first. The succeeding crystallisations were shaken with ammonia and chloroform; a new alkaloid, anhalamine, remained undissolved. The alkaloids which dissolved were converted into hydrochlorides and heated with absolute alcohol; the hydrochloride of mezcaline went into solution, whilst that of anhalonidine remained undissolved.

*Anhalamine* melts at  $186^\circ$ , and is a strong base. It dissolves to

some extent in boiling chloroform and benzene, and the solutions solidify to a gelatinous mass as they cool. C. F. B.

**Derivatives of Ecgonine.** By RICHARD WILLSTÄTTER (*Ber.*, 1899, 32, 1635—1641).—The *aurichloride* of ethylic ecgonine methochloride is very slightly soluble in water, and crystallises in prisms melting at 176—177°. The *aurichloride* of ecgonine methochloride crystallises in thin flakes and melts with decomposition at 214—217°; it is somewhat soluble in hot water and on cooling separates with 1H<sub>2</sub>O.

Unlike ethylic ecgonine, its methiodide is not hydrolysed by boiling with water during 12 hours. Silver oxide, however, converts it into *ecgonine methylbetaine*, which crystallises in slender, colourless prisms, decomposes and melts at 278°, dissolves sparingly in water, very slightly in hot alcohol, and is insoluble in ether. By the action of concentrated hydriodic acid, the betaine is converted into *ecgonine methiodide*, a monobasic acid, which dissolves readily in water, crystallises in prisms, and decomposes at 238—239°.

*Methylic dihydroxyanhydroecgonine methiodide* melts and decomposes at 205—206°; it crystallises in four-sided prisms or six-sided tablets, and is very readily soluble in cold water; no trace of dimethylamine is eliminated, even after long boiling with strong potash. *Dihydroxyanhydroecgonine methiodide* decomposes at 255°, dissolves easily in water, but only slightly in boiling alcohol, and crystallises in square tablets; it is a monobasic acid, and does not form a lactone.

*Dihydroxyanhydroecgonine methylbetaine* resembles ecgonine methylbetaine; it is very easily soluble in water and slightly soluble in alcohol, from which it crystallises in tablets and tetragonal pyramids; it decomposes between 260° and 270°, is slightly hygroscopic, and has a neutral reaction.

In reply to Buchner (this vol., i, 423), it is suggested that the variation in melting point of the amide of  $\Delta^1$ -cycloheptenecarboxylic acid, when prepared in different ways, is due to different degrees of purity and not to *cis*- and *trans*-, or to structural isomerism. Conductivity determinations gave for this acid  $\mu_{\infty} = 375$ ,  $100k = 0.000830$ , whilst  $\gamma$ -cycloheptatrienecarboxylic acid (m. p. 55°, from ecgonine) gave  $\mu_{\infty} = 377$ ,  $100k = 0.00379$ , and the  $\delta$ -acid (m. p. 32°, from anhydroecgonine) gave  $\mu_{\infty} = 377$ ,  $100k = 0.00396$ . T. M. L.

**Emetine Octiodide; Extraction and Estimation of Alkaloids.** By HARRY MANN GORDIN and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1899, 21, 231—239).—The authors have applied their iodometric method for the estimation of alkaloids (*Abstr.*, 1898, i, 707) to the assay of nux vomica, belladonna root and leaves, and ipecacuanha root. Emetine octiodide is a dark brown powder, scarcely soluble in benzene, ether, or chloroform, moderately soluble in alcohol, and very readily in a mixture of four parts of alcohol with one part of chloroform. The formula assigned to it is C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>O<sub>5</sub>.HI<sub>7</sub>, corresponding with Lefort and Wurtz's formula for emetine (this Journal, 1877, ii, 628). T. M. L.

**Pelosine.** By MAX SCHOLTZ (*Arch. Pharm.*, 1899, 237, 199—200).—The pelosine obtained from *Radix Pureiræ bravae* by extraction

with water containing sulphuric acid and precipitation with sodium carbonate, is shown to be identical with bebeerine (this vol., i, 92).  
C. F. B.

**Staphisagroine, a New Alkaloid.** By FELIX B. AHRENS (*Ber.*, 1899, 32, 1581—1584 and 1669—1670).—After the extraction of the alkaloids delphinine, delphinoidene, delphisine, and staphisagrine from the seeds of *Delphinium staphisagria* by means of chloroform, a small quantity of a substance insoluble in this solvent remains behind. This alkaloid, to which the author gives the name *staphisagroine*,  $C_{40}H_{46}N_2O_7$ , is a faintly yellow, amorphous powder which melts at  $275$ — $277^\circ$ , and is practically insoluble in all the usual solvents; it dissolves in dilute hydrochloric acid, from which solution it is reprecipitated on adding ammonia. It yields a *picrate* insoluble in hot alcohol, melting and decomposing at  $215$ — $216^\circ$ . The *aurichloride* is yellow, insoluble, and amorphous, darkening at  $180^\circ$ , and remaining unmelted at  $275^\circ$ . The *platinochloride* is light yellow and amorphous, and does not melt at  $275^\circ$ .

An attempt to reprepare the alkaloid by decomposing the platinochloride with hydrogen sulphide gave rise to another alkaloid, *staphisagroidine*,  $C_{40}H_{40}N_2O_4$ , a brownish powder which melts at  $185^\circ$ ; the amorphous *aurichloride* remains unmelted at  $270^\circ$ .

Staphisagroine does not give any of the colour reactions characteristic of the delphinium alkaloids.  
J. F. T.

**Pectins.** By ÉMILE BOURQUELOT (*Compt. rend.*, 1899, 128, 1241—1244. Compare Abstr., 1898, i, 607).—Pectins are substances which dissolve in water, forming viscid solutions which resemble those of the gums and mucilages in yielding mucic acid by oxidation with nitric acid, and differ from them in being coagulated by barium and calcium hydroxides and the soluble ferment pectase; moreover, the pectins yield pectic acid on treatment with potash. The author has isolated pectins from the quince, rose de Provins, and *Cynorrhodon*, and a variety of gooseberry (*Groseille à maquereau*), by extracting the vegetable matter with alcohol, digesting with water at  $108$ — $110^\circ$ , and precipitating the pectin from the aqueous solution by alcohol. The four pectins thus obtained, and that from gentian root are, contrary to Fremy's observation, optically active; they are all dextrorotatory, the value of  $\alpha_D$  varying from  $82.3^\circ$  to  $194^\circ$ . They yield arabinose on hydrolysis with dilute sulphuric acid, and mucic acid on oxidation with nitric acid; it appears probable therefore that they are derived in part from araban and galactan, although only in the case of the pectin from gentian has a product resembling galactose been obtained on hydrolysis.

Germinated barley contains a soluble ferment capable of hydrolysing pectins, and as this is absent in the saliva and in the juice of *Aspergillus niger*, it cannot be amylase which occurs in these fluids; in all probability, it is a new ferment and the name *pectinase* is suggested for it. When pectinase is added to a solution of pectin, the latter is no longer coagulable by pectase and a reducing sugar is produced; moreover, the ferment has the power of dissolving the coagulum produced by pectase, the action being one of hydrolysis. On adding the two

ferments simultaneously to a solution of pectin, a coagulum appears and afterwards redissolves if the pectase is in excess; if, however, the pectinase predominates, the solution remains clear. The effects of pectase and pectinase on pectins are quite comparable with those of rennet and trypsin on casein; in each case, the former ferment coagulates whilst the latter redissolves the coagulum. G. T. M.

**Pectin Present in Gooseberry.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1899 [vi], 6, 281—286).—The pectin was obtained from the crushed gooseberries by a method analogous to that employed for the extraction of pectin from gentian root (Abstr., 1898, i, 607). It is completely soluble in water, the solution being dextrogyrate  $[\alpha]_D + 194.1^\circ$ . A 1 per cent. solution of the pectin is coagulated by a solution of pectase, this occurring more readily if a little precipitated chalk be added; it is also gelatinised by lime water, baryta water, lead acetate, &c.; the sulphates of magnesium and ammonium precipitate it from its solution, but sodium sulphate does not. When heated with nitric acid of sp. gr. 1.15, the pectin yields mucic acid, and when heated under pressure at 105—110° with 2 per cent. sulphuric acid, arabinose is produced. After treatment with malt diastase, the pectin solution is no longer coagulated by a solution of pectase; this change is believed to be due to the action of a ferment present in the diastase for which the name "*pectinase*" is proposed (compare preceding abstract). H. R. LE S.

**Oxidising Ferments in Aconite and Belladonna.** By E. LÉPINOIS (*J. Pharm.*, 1899 [vi], 2, 49—52).—The roots and leaves of aconite and belladonna contain an oxidising ferment (oxydase), which is similar to those studied by Bertrand and others (compare Brisse-moret and Joanne, this vol., ii, 319). The ash contains small quantities of iron and manganese. When exposed to air, the ferment absorbs oxygen, and carbonic anhydride is produced. H. R. LE S.

**Constitution of the Proteid Molecule.** By FR. PRÖSCHER (*Zeit. physiol. Chem.*, 1899, 27, 114—122).—The products of decomposition of hæmoglobin brought about by hydrochloric acid were estimated, but only about half the nitrogen, carbon, and oxygen and two-thirds of the hydrogen were accounted for. W. D. H.

**The Nitrogen in the Proteid Molecule,** By WALTHER HAUSMANN (*Zeit. physiol. Chem.*, 1899, 27, 95—108).—The differences between different proteids, so far as nutrition is concerned, is associated with a fundamental chemical difference in the way in which their nitrogen is combined, as evinced by the nature of the products of decomposition by acids. These products may, by their chemical behaviour, be divided into three categories, which admit of estimation without separation of the individual constituents, and the nitrogen so obtained may be termed (1) amidic nitrogen, (2) diamino-nitrogen (from diamino-acids, &c., such as lysine, arginine, and histidine), (3) monamino-nitrogen (from compounds such as leucine, tyrosine, aspartic and glutamic acids, &c.).

The following table gives the results of determinations made in this manner :—

	Amidic nitrogen, per cent.	Diamino- nitrogen, per cent.	Monamino- nitrogen, per cent.	Total.
Crystallised egg-albumin...	8.53	21.33	67.80	97.66
Crystallised serum-albumin	6.34	—	—	—
Serum-globulin .....	8.90	24.95	68.28	102.13
Casein .....	13.37	11.71	75.98	101.06
Gelatin .....	1.61	35.83	62.56	100.00

W. D. H.

**Action of Formaldehyde on Proteids.** By CHARLES LEPIERRE (*Compt. rend.*, 1899, 128, 739—742).—The author has investigated the action of formaldehyde on the heteroalbumoses, protalbumoses, deuterioalbumoses, and peptones prepared by the artificial digestion of egg-albumin, fibrin, muscle, and gelatin. At the ordinary temperature, there is little or no action, but at 100° there is energetic reaction, the substance being precipitated, or being materially changed without becoming insoluble.

Protalbumoses are precipitated by formaldehyde from hot solutions, and the product is insoluble in hot water or in a 10 per cent. sodium chloride solution, or in sodium carbonate solution. Deuterioalbumoses of high molecular weight are precipitated by formaldehyde, whilst those of low molecular weight are converted into protalbumoses, and the latter by further action of the reagent are precipitated. The true peptones are first converted into deuterioalbumoses, and the latter are subsequently changed into protalbumoses in the manner just indicated.

When the products of the action of formaldehyde are heated for an hour or two at 110°, they become hydrated, dissolve completely, and are converted into proteids of the same character as the original substance.

The albumoses and peptones precipitated by formaldehyde are capable of slow digestion by pepsin, and therefore are not, as Trillat supposed, incapable of being assimilated.

It will be seen that the action of formaldehyde is closely analogous to the gradual retrogression of peptones and albumoses to the original proteids of high molecular weight.

C. H. B.

**Globulin of White of Egg.** By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1898, ii, 358; from *J. Russ. Chem. Soc.*, 1898, 29, 22—27).—Globulin is prepared by diluting fresh white of hen's egg with 1/3—1/4 its volume of water, adding an equal volume of a saturated solution of ammonium sulphate to the filtrate, and leaving the mixture for a month; the precipitate is then pressed between filter paper, and extracted with a half-saturated solution of ammonium sulphate. After a week's exposure in a flat dish, a precipitate consisting of minute needles is formed; these have a specific rotatory power  $[\alpha]_D - 23.9^\circ$ . A substance crystallising in small needles is also obtained by freezing white of egg and then treating with ammonium sulphate as before



its specific rotatory power is  $[\alpha]_D -24.2^\circ$ . Globulin hydrochloride, prepared by dialysing the crystalline globulin into a 0.2 per cent. solution of hydrochloric acid, has the composition C=50.80, H=7.392, N=15.13, Cl=2.84, S=1.66, and a specific rotatory power  $[\alpha]_D -41.8-51.9$ . The solution obtained by heating for two hours with a 0.2 per cent. solution of hydrochloric acid has a specific rotatory power  $[\alpha]_D -79.56^\circ$ , and the precipitate formed from it, by adding alcohol and ether, is easily soluble in hot water, and contains 60.56 C, 6.58 H, 14.65 N, 2.58 Cl, and 1.6 S. The properties and behaviour of the crystalline globulin are identical with those of crystalline albumin, and egg-globulin may be regarded as a mixture of the latter with an unknown compound. E. W. W.

**Albumins of White of Egg.** By ALEXEI A. PANORMOFF (*Chem. Centr.*, 1898, ii, 487—488; from *J. Russ. Chem. Soc.*, 1898, 30, 302—310).—Besides the crystalline albumin obtained from white of hen's egg by Hofmeister's method, an amorphous albumin may be separated by fractionally precipitating the solution in saturated ammonium sulphate solution, and fractionally dissolving the precipitate in a half-saturated solution of the sulphate until the product attains a constant specific rotatory power. This albumin (II) separates in globular masses, which become pink at the ordinary temperature and are stable only below  $10^\circ$ ; it gives the reactions of white of egg, and has the properties of an acid derivative. When dialysed in ammonium sulphate solution, the specific rotatory power is  $[\alpha]_D -36.2^\circ$ , that of the crystalline albumin (I) being  $23.6^\circ$ ; and when dialysed in water at  $0-5^\circ$ , it yields a faintly pink, acid solution. The molecular weight is calculated to be 3358. The hydrochloride contains 3HCl, has a specific rotatory power  $[\alpha]_D -54.8^\circ$ , is easily soluble in water, and is precipitated by alcohol and ether. When heated in a sealed tube with a 0.1 per cent. solution of hydrochloric acid for  $1\frac{1}{4}$  hours, its specific rotatory power increases to  $-63.5^\circ$ , although its composition remains practically unchanged. The hydrobromide contains 2HBr, and has the specific rotatory power  $[\alpha]_D -53^\circ$ , rising to  $-63.5^\circ$  when heated with acid. The phosphate contains  $5H_3PO_4$  to 2 mols. of albumin, and when dialysed in a 0.2 per cent. solution of phosphoric acid has a specific rotatory power  $[\alpha]_D -52.5^\circ$ . White of egg probably only contains the albumins (I) and (II), for the specific rotatory powers of the hydrochlorides, hydrobromides, and phosphates, prepared directly from it, correspond within limits of errors of experiment with the mean of the values obtained for the corresponding compound of each albumin. E. W. W.

**Action of Dilute Solutions of Pyrophosphoric Acid on the Crystalline Albumin of White of Egg.** By WLADIMIR WORMS (*Chem. Centr.*, 1898, ii, 488; from *J. Russ. Chem. Soc.*, 1898, 30, 310—319).—Preparations of the crystalline albumin (I) of white of egg, freed from ammonium sulphate by dialysing into water, were treated with pyrophosphoric acid until the acid reaction was shown with tropæolin OO and were then dialysed into 0.05, 0.2, and 0.5 per cent. solutions of pyrophosphoric acid. The three solutions showed the same properties and had the specific rotatory power  $[\alpha]_D -26.1^\circ$ ,

but since the precipitates obtained by adding 95 per cent. alcohol to the more concentrated solutions of pyrophosphoric acid have a greater content of phosphorus, this acid, like orthophosphoric acid, probably forms several different compounds with the albumin. When the solutions of the albumin pyrophosphates are heated in a closed tube at  $100^{\circ}$ , the properties of the liquids, and the composition of the precipitates obtained from these by adding alcohol and ether, show that the pyrophosphates have become orthophosphates, although the specific rotatory power of the precipitates is  $[\alpha]_D - 67.5^{\circ}$ , whilst that of the corresponding orthophosphates is  $-58.8^{\circ}$ . E. W. W.

**Products of the Action of Pepsin and Pancreatic Juice on Fibrin.** By V. HARLAY (*J. Pharm.*, 1899, [vi], 5, 225—232).—The digestive action of pepsin or pancreatic juice on fibrin has, until now, been regarded as ended when the filtered liquid gives no turbidity with nitric acid; this is shown to be incorrect, as by continuing the digestion beyond this stage, tyrosine crystals were obtained, and the rotatory power of the solution was found to go on diminishing in value. The colour change from red to black produced by the juice of *Russula delica* is characteristic of tyrosine, and is given by the solution obtained by the action of pepsin on fibrin, whereas a red coloration changing to green is produced if the fibrin is digested with pancreatic juice. H. R. LE S.

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## Organic Chemistry.

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**Chemical Action of the Silent Electric Discharge on Carbon Compounds.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, [vii], 16, 5—103).—A detailed account of work already published (compare Abstr., 1897, i, 330; 1898, i, 393, 551, 554, 558, and 594). G. T. M.

**Conversion of Trimethylene into Propylene.** By SIMEON M. TANATAR (*Ber.*, 1899, 32, 1965—1967. Compare Abstr., 1896, i, 457, and this vol., i, 422).—When a mixture of trimethylene and propylene is rapidly (6—7 litres per hour) bubbled through well-cooled bromine, practically the whole of the trimethylene passes through unaltered, whilst the propylene is completely absorbed, forming propylenic bromide. This difference affords an easy method for the complete conversion of trimethylene into propylene. The trimethylene is passed through a hot tube and then through bromine, the unabsorbed gas is passed through the hot tube again and then through the bromine, and these processes are repeated until practically the whole of the gas is absorbed. A control experiment proved that trimethylene itself, when passed through bromine, does not yield propylenic bromide.

J. J. S.

**Absorption of Hydrogen Phosphide in Presence of Alkali Chlorides and the Purification of Crude Acetylene.** By CHRISTIAN GÖTTIG (*Ber.*, 1899, 32, 1879—1882).—On passing acetylene containing hydrogen phosphide into an aqueous solution of a mixture of cupric chloride with an alkali chloride, copper phosphide,  $\text{Cu}_3\text{P}_2$ , is formed, but the precipitation of copper acetylides is not prevented. The presence of an alkali chloride, however, prevents a solution of mercuric chloride from uniting with acetylene to form an explosive compound, although its power of absorbing hydrogen phosphide is increased; during this absorption, a white substance separates which probably consists of mercury phosphide, combined with mercuric phosphate, and there is also formed a yellow compound,  $3\text{Hg}_3\text{P}_2, 7\text{HgCl}_2$ , a red compound,  $4\text{Hg}_3\text{P}_2, \text{HgCl}_2$ , and a brown compound,  $\text{Hg}_3\text{P}_2, \text{HgCl}_2$ .

The conclusion is drawn that the absorption of hydrogen phosphide present in acetylene by solutions of easily reducible metallic salts is increased by the presence of a chloride of an alkali metal, whilst the need of using acids to prevent the formation of explosive metallic compounds of acetylene is obviated. W. A. D.

**Copper Acetylides.** By MARTIN FREUND and LUDWIG MAI (*Chem. Centr.*, 1899, i, 410—411; from *Acetylen in Wiss. u. Ind.*, 1898, 285—286).—When copper acetylides dried at 50—60° is placed in a tube through which acetylene is passed, it explodes after a short time, but does not cause the explosion of the acetylene. The copper acetylides are themselves only explosive when they have been exposed to the action of oxygen or air in the process of drying. E. W. W.

**Allene Hydrocarbons.** By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1899, [ii], 59, 517—542).—The allene hydrocarbons are prepared by

the action of alcoholic potash on the corresponding keto-dichlorides. *β*-Diethylallene,  $\text{C}(\text{Et})_2:\text{C}:\text{CH}_2$ , prepared from the chloride derived from diethylacetone, is a colourless, strongly refractive liquid which boils at  $96-98^\circ$ , and has a sp. gr.  $0.7475$  at  $0^\circ/0^\circ$ . On treatment with hydrogen bromide in acetic acid solution, it gives *α*-bromo-*γ*-ethylpentylene,  $\text{C}(\text{Et})_2:\text{CH}\cdot\text{CH}_2\text{Br}$ , which boils at  $152-154^\circ$ , has a sp. gr.  $1.2079$  at  $0^\circ/0^\circ$ ; and *αγ*-dibromo-*γ*-ethylpentane,  $\text{CBrEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , boiling at  $109-110^\circ$ , and of sp. gr.  $1.5799$  at  $0^\circ/0^\circ$ . By the action of alcoholic potash on the latter, there are obtained *β*-diethylallene and ethylic *β*-diethylallylic ether,  $\text{C}(\text{Et})_2:\text{CH}\cdot\text{CH}_2\cdot\text{OEt}$ , which boils at  $156-158^\circ$ , and has a sp. gr.  $0.8290$  at  $0^\circ/0^\circ$ .

*β*-Methylethylallene,  $\text{CMeEt}:\text{C}:\text{CH}_2$ , prepared from the chloride of methylethylacetone, is a very strongly refractive, transparent liquid boiling at  $70-71^\circ$ , and of sp. gr.  $0.7310$  at  $0^\circ/0^\circ$ . With hydrogen bromide, it gives *αγ*-dibromo-*γ*-methylpentane,  $\text{CMeEtBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , which boils at  $94-96^\circ$ , and has a sp. gr.  $1.6360$  at  $0^\circ/0^\circ$ . On treatment with alcoholic potash, this compound is converted into *β*-methyl-ethylallene and ethylic *β*-methylethyl allylic ether; the latter boils at  $141-143^\circ$ , and has a sp. gr.  $0.8208$  at  $0^\circ/0^\circ$ .

By the action of alcoholic potash on trimethyltrimethylenic dibromide,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CHMeBr}$ , an unsaturated ether is obtained, probably having the formula  $\text{CMe}_2:\text{CH}\cdot\text{CHMe}\cdot\text{OEt}$ , which boils at  $124-126^\circ$ , and has a sp. gr.  $0.8084$  at  $0^\circ/0^\circ$ .

The various allene hydrocarbons can be distinguished by treatment with hydrogen bromide and subsequently with alcoholic potash: (i) Mono-substituted allenes give dibromotrimethylenes (compare Patieff, Abstr., 1896, i, 330),  $\text{R}\cdot\text{CH}:\text{C}:\text{CH}_2 + 2\text{HBr} = \text{R}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ . These, with alcoholic potash, give unsaturated primary mono-substituted ethylic allylic ethers,  $\text{R}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br} \rightarrow \text{R}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{OEt}$ ; (ii) *β*-di-substituted allenes give *β*-di-substituted dibromotrimethylenes  $\text{CR}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , from which unsaturated primary *β*-di-substituted ethylic allylic ethers,  $\text{CR}_2:\text{CH}\cdot\text{CH}_2\cdot\text{OEt}$ , can be obtained; (iii) tri-substituted allenes give tri-substituted dibromotrimethylenes,  $\text{CR}_2\text{Br}\cdot\text{CH}_2\cdot\text{CHRBr}$ , which yield unsaturated secondary tri-substituted ethylic allylic ethers,  $\text{CR}_2:\text{CH}\cdot\text{CHR}\cdot\text{OEt}$ ; (iv) tetra-substituted allenes give tetra-substituted dibromotrimethylenes,  $\text{CR}_2\text{Br}\cdot\text{CH}_2\cdot\text{CBrR}_2$ , which, with alcoholic potash, yield the original hydrocarbon. R. H. P.

**Formation of Cuprous Cyanide.** By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 261—262).—By heating a mixture of copper acetate and aqueous ammonia for two hours in a sealed tube at  $180-185^\circ$ , a colourless liquid is obtained containing in suspension finely divided copper and a white precipitate consisting of crystalline plates. On filtering the liquid, which immediately turns blue, and removing the copper from the precipitate by digesting it with very dilute sulphuric acid, the residual crystalline plates are found to consist of cuprous cyanide. On mixing the blue filtrate with alcohol and placing it in a desiccator, blue needles of copper carbonate are deposited. T. H. P.

**Substituted Cyanamides and Thiocarbamides.** By OTTO WALLACH (*Ber.*, 1899, 32, 1872—1875).—The following di-substituted

cyanamides have been prepared by the action of cyanogen bromide (1 mol.) on an ethereal solution of the secondary amine (2 mols.). *Cyanodimethylamine*,  $\text{CN} \cdot \text{NMe}_2$ , is an oil boiling at  $52^\circ$  under 14 mm. pressure. *Cyanodiethylamine*,  $\text{CN} \cdot \text{NEt}_2$ , is an oil boiling at  $68^\circ$  under 10 mm. pressure. *Cyanodipropylamine*,  $\text{CN} \cdot \text{NPr}_2$ , is an oil boiling at  $88\text{--}90^\circ$  under 10 mm. pressure. *Cyanodiamylamine*,  $\text{CN} \cdot \text{N}(\text{C}_5\text{H}_{11})_2$ , is an oil boiling at  $130\text{--}132^\circ$  under 10 mm. pressure. *Cyanopiperidine*,  $\text{CN} \cdot \text{C}_5\text{NH}_{10}$ , is an oil boiling at  $102^\circ$  under 10 mm. pressure. *Cyanodibenzylamine*,  $\text{CN} \cdot \text{N}(\text{CH}_2\text{Ph})_2$ , melts at  $54^\circ$  and boils at  $145\text{--}148^\circ$  under 10 mm. pressure. *Cyanomethylaniline*,  $\text{CN} \cdot \text{NMePh}$ , melts at  $28^\circ$  and boils at  $136^\circ$  under 10 mm. pressure. Unlike cyanamide and the monalkylcyanamides, these substances have no tendency to polymerise. By saturating an alcoholic solution with ammonia and hydrogen sulphide, they are converted into the corresponding thiocarbamides, some of which have already been prepared by isomeric change from the thiocyanates, as is shown in the following table :

Base.	Melting point.	
$\text{NH}_2 \cdot \text{CS} \cdot \text{NMe}_2$ .....	158—159°	{ 159° H. Salkowski. 81—82° Spica and Carrara.
$\text{NH}_2 \cdot \text{CS} \cdot \text{NEt}_2$ .....	101—102	169—170° Spica and Carrara.
$\text{NH}_2 \cdot \text{CS} \cdot \text{NPr}_2$ .....	67	—
$\text{NH}_2 \cdot \text{CS} \cdot \text{N}(\text{C}_5\text{H}_{11})_2$ .....	63—64	208—209° Spica and Carrara.
$\text{NH}_2 \cdot \text{CS} \cdot \text{NC}_5\text{H}_{10}$ .....	128	—
$\text{NH}_2 \cdot \text{CS} \cdot \text{N}(\text{CH}_2\text{Ph})_2$ .....	139—140	139—140° H. Salkowski.
$\text{NH}_2 \cdot \text{CS} \cdot \text{NMePh}$ .....	106—107	107° Gebhardt.

T. M. L.

**Etherification of Phosphoric Acid by the Aid of Methylic Alcohol.** By GUILLAME BELUGOU (*Bull. Soc. Chim.*, 1899, [iii], 21, 166—169).—The conclusions arrived at are :—(1) That by the action of phosphoric acid on methylic alcohol the limit of etherification is instantaneously reached, and that this limit is independent of the manner in which the acid and alcohol are mixed. (2) That an increase in temperature or time serves to diminish the coefficient of etherification until it reaches a minimum of about 10 per cent., when it gradually increases again. (3) That the presence of minute quantities of water diminishes the rate of etherification to a very appreciable extent. Preliminary experiments proved that the product is a monomethylic phosphate.

J. J. S.

**Behaviour of Isomeric Alcohols with Phosphorus Trichloride.** By TH. MILOBENSKI (*Chem. Centr.*, 1899, i, 249; from *J. Russ. Chem. Soc.*, 1898, 30, 730—734).—According to Jaroschenko (*ibid.*, 29, 223), by the action of phosphorus trichloride on secondary alcohols, olefines, and sometimes small quantities of alkylic chlorides, are formed. The author finds, however, that by the action of phosphorus trichloride on isopropylic alcohol, di-isopropylic phosphite, isopropylic chloride, hydrogen chloride, and a very small quantity of propylene are obtained. The product of the reaction, when distilled under the

ordinary pressure, yields only isopropyl chloride. *Di-isopropyl phosphite*,  $\text{P(OPr)}_2\text{OH}$ , is a limpid liquid, boils at  $72-73^\circ$  under 6.5 mm., at  $76-77^\circ$  under 10 mm., and at  $85-86^\circ$  under 17 mm. pressure. The silver salt, prepared by means of a concentrated solution of silver nitrate containing a few drops of ammonia, is a white, amorphous substance. E. W. W.

**Preparation of Ethylenic Glycol.** By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 221—227).—When powdered caustic potash is added to glycol diacetate, rapid action occurs, and on distilling under reduced pressure, a 90 per cent. yield of glycol is obtained; an equally good yield of propylenic glycol can be obtained in similar manner from its acetate. Since the potassium acetate, formed in these cases, fuses during distillation and frothing occurs, the method is improved by using baryta or, better, dry powdered calcium hydroxide to effect the hydrolysis; under these conditions, no frothing occurs during distillation and the yield is 93 per cent. of the theoretical. W. A. D.

**Oxidation of Trichlorethoxyethylene.** By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 215—220).—When trichlorethoxyethylene,  $\text{CCl}_2\text{:CCl}\cdot\text{OEt}$ , is exposed to moist air, it is converted into oxalic acid, hydrogen chloride being evolved; the same is true of the corresponding trichloromethoxyethylene. On passing a stream of dry oxygen, however, over trichlorethoxyethylene, it is converted into a colourless, fuming liquid, which the author has previously assumed to be dichlorethoxyacetic chloride,  $\text{OEt}\cdot\text{CCl}_2\cdot\text{COCl}$  (Abstr., 1879, 231). When distilled, under atmospheric pressure, the larger part of this substance passes over at  $140^\circ$ , although portions distil between  $100^\circ$  and  $140^\circ$ , and  $140^\circ$  and  $200^\circ$ . Since the compound,  $\text{OEt}\cdot\text{CCl}_2\cdot\text{COOEt}$ , obtained by acting on ethylic oxalate with phosphorus pentachloride (Anschütz, Abstr., 1890, 236), boils, under atmospheric pressure, at the same temperature as ethylic oxalate, the author concludes that the compound  $\text{OEt}\cdot\text{CCl}_2\cdot\text{COCl}$  would have approximately the same boiling point, about  $140^\circ$ , as ethyloxalic chloride,  $\text{COOEt}\cdot\text{COCl}$ , and his former assumption as to the nature of the oxidation product of trichlorethoxyethylene is justified. It is probable that the portion which distils below  $140^\circ$  consists largely of oxalic chloride, formed by the decomposition of dichlorethoxyacetic chloride; whilst the fraction boiling above  $140^\circ$  probably contains ethylic hydrogen oxalate, formed by moisture present in the oxygen acting on the original trichlorethoxyethylene. The author intends returning to the subject. W. A. D.

**Glycerophosphoric Acid.** By JACQUES CAVALIER and POUGET (*Bull. Soc. Chim.*, 1899, [iii], 21, 364—366).—Calcium glycerophosphate, like the alkaline earth salts of the various monalkylphosphoric acids, is less soluble in hot than in cold water. The weight of the anhydrous salt contained in 100 grams of the saturated aqueous solution was found to be 7.9 grams at  $16^\circ$ , 4.4 grams at  $36^\circ$ , 2.3 grams at  $51^\circ$ , 1.3 grams at  $77^\circ$ , 1.25 grams at  $86^\circ$ , and 1.15 grams at  $100^\circ$ . On boiling the cold, saturated solution, the greater part of the salt is deposited, and its purification is better effected by this means than by precipitation with alcohol. Calcium glycerophosphate is comparable as regards

stability with calcium ethyl- and methyl-phosphates, a hot, saturated solution of the salt acquiring only a slight opalescence when heated at 95° for 3 hours. The barium salt is less stable, and on this account, and also because its solubility varies less with the temperature, its purification is better effected by precipitation with alcohol. At the ordinary temperature, a saturated solution contains 4·5 per cent. of the salt, which is reduced to 3 per cent. on boiling.

Glycerophosphoric acid, in presence of phosphoric acid, may be estimated by the process previously described (this vol., ii, 55) for the estimation of alkyl phosphates, but the results are not quite so satisfactory as in the latter case. The hydrolysis of the acid, which was studied in the case of a 0·1 normal solution at 88°, obeys the law for monomolecular reactions, and the velocity of decomposition increases rapidly with rise of temperature. Comparison of the value (0·0058) found for  $k$  in the equation  $x = e^{-kt}$ , that is, for the amount of acid decomposed in one hour under the above conditions, with the corresponding values for methylphosphoric (0·0056), ethylphosphoric (0·0032), and allylphosphoric (0·0055) acids shows that the stability of glycerophosphoric acid is much less than that of ethylphosphoric acid but practically equal to that of methyl- and allyl-phosphoric acids.

N. L.

**Action of Alkalis on the Sugars.** VI. Maltose, Lactose, and Melibiose. By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 147—149. Compare Abstr., 1898, i, 225 and 227).—When a 20 per cent. aqueous solution of maltose is heated with one-fifth its volume of normal caustic potash for 3 hours at 100°, dextrose is initially formed, but undergoes conversion into mannose, which can be isolated in the form of its phenylhydrazone. On fermenting the solution, a residue remains which has a dextrorotatory power nearly one-half that of dextrose; this residue, which is converted into dextrose by the action of dilute acid, and thus rendered fermentable, appears to consist of an anhydride of dextrose.

Lactose, on treatment with alkali, yields galactose, which can be isolated in the form of its phenylmethylhydrazone; a small quantity of  $\psi$ -tagatose is also formed, but neither dextrose nor mannose can be isolated; dextrose, if formed, appears to exist as anhydride. Lead hydroxide converts lactose into the same products as caustic potash.

Melibiose, under the influence of potash or lead hydroxide, yields galactose; the formation of dextrose could not be proved.

Fischer has shown that the aldehyde-group of lactose is in that portion of the molecule which, on inversion, yields dextrose; the authors' experiments indicate, on the contrary, that this group is in the portion which gives rise to galactose. The apparent contradiction awaits explanation.

W. A. D.

**Compounds Formed by Polyhydric Alcohols with Benzaldehyde.** By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 150—152).—The following table gives the properties of the products formed by the condensation of certain polyhydric alcohols with benzaldehyde.

Name.	Melting point. °F.	Specific rotatory power $[\alpha]_D$			Solubility (milligrams) in 10 c.c. at 16–18°.			Completely decomposed after boiling with 20 times its weight of normal $H_2SO_4$ for
		for 0.25–0.5 per cent. solutions.	of the free alcohols (0.5 per cent.) with ammonium molybdate.		Acetone.	Chloroform.	Alcohol.	
			6.75/24 mol.	After adding 2 c.c. normal $H_2SO_4$ per 25 c.c.				
Dibenzylidene-erythritol .....	201°	0° (chloroform)	0°	0°	34	364	2	—
Monobenzylidene-arabitol .....	152	—	–42	–94	—	—	—	—
Dibenzylidene-adonitol .....	165	0	0	0	64	136	14	—
Dibenzylidenexylitol .....	175	0	—	—	110	85	—	—
Dibenzylidenesorbitol .....	203	–55	–43	–115	70	255	110	1½ hours
Monobenzylidene- $\alpha$ -sorbitol .....	175	+6 (alcohol)	—	—	very easily	easily	soluble	—
Dibenzylidene- $\alpha$ -sorbitol .....	163	+29 (acetone)	+41	+90	544	16	10	½ hour
Tribenzylidenemannitol .....	213–218	–13 (chloroform)	+43	+120	42	875	10	8 hours
Tribenzylidene- $\beta$ -iditol*	215–218	–6 (acetone)	+107	+37	47	17	5	2 hours
Tribenzylidene- $\alpha$ -talitol† .....	210	–40 (chloroform)	+60	+8	30	442	traces	6 hours
Dibenzylidenedulcitol .....	215–220	0	0	0	42	83	traces	—
Dibenzylidenepseitol .....	230–235	–60 (acetone)	+48	+132	4	traces	2	—

\* Prepared from *l*-idonic acid.† Prepared from *d*-talonic acid.

W. A. D.



**Action of Aqua Regia on Fatty Primary Amines.** By WASSILY A. SOLONINA (*Chem. Centr.*, 1899, i, 254; from *J. Russ. Chem. Soc.*, 1898, 30, 822—825).—By the action of a mixture of 4 parts of hydrochloric acid of sp. gr. 1.16 with 1— $1\frac{1}{2}$  of nitric acid of sp. gr. 1.4 on salts of hexamethylenediamine, dichlorohexane and a compound containing more chlorine were obtained, and the product of the reaction, when treated with sodium phenoxide, yielded *aa'*-diphenoxyhexane melting at 82.5° and other substances which were not identified. Salts of octomethylenediamine with aqua regia also form chlorine compounds, and by treating the product with sodium phenoxide *aa'*-diphenoxyoctane was prepared. By the action of aqua regia on benzylamine and isobutylamine, benzylic and isobutylic chlorides were respectively obtained, together with other liquid and solid products. E. W. W.

**Composition of Nitrogen Iodide and the Action of Iodine on Fatty Amines.** By JAMES F. NORRIS and ARTHUR I. FRANKLIN (*Amer. Chem. J.*, 1899, 21, 499—509. Compare Chattaway, *Trans.*, 1898, 69, 1572).—On mixing ethereal solutions of iodine and triethylamine at ordinary temperatures or at  $-3^\circ$ , an oil separated which had the composition of a *periodide*,  $\text{NEt}_3\text{I}_2$ , and yielded hydrogen iodide when treated with concentrated sulphuric acid; the mother liquor contained triethylamine hydriodide; similar results were obtained when carbon tetrachloride was used as the solvent. In dilute aqueous solution, iodoform was precipitated, but in concentrated solution, the oily *periodide* was formed. No indication was observed of the formation of an additive product,  $\text{NEt}_3\text{I}_2$ , comparable to those obtained from trimethylamine and tripropylamine.

On mixing ethereal solutions of tripropylamine and iodine, an oil was obtained which gradually deposited stout, prismatic crystals of the *iodide*  $\text{NPr}_3\text{I}_2$ ; these melted at  $66^\circ$ , and were not acted on by concentrated sulphuric acid; the compound is insoluble in ether, slightly soluble in carbon tetrachloride, soluble in ethylic acetate or chloroform, and in contact with water melts to an oil. With carbon tetrachloride as solvent, an oil was obtained together with crystals of tripropylamine hydriodide. In aqueous solution, an oil was precipitated having the composition of the *periodide*,  $\text{NHPr}_3\text{I}_2$ .

On mixing ethereal solutions of diethylamine and iodine, a dark oil was precipitated which yielded hydrogen iodide when treated with sulphuric acid, and was therefore not a direct additive product; diethylamine hydriodide is also formed. Similar results were obtained with carbon tetrachloride as a solvent; in dilute aqueous solution, in presence of sodium carbonate, iodoform was produced; in the absence of any solvent, a violent reaction takes place, accompanied by much heat and the evolution of white fumes, but at  $-18^\circ$  the two substances were inactive.

On mixing ethereal solutions of diamylamine and iodine, a black, crystalline *periodide*,  $\text{NH}_2(\text{C}_6\text{H}_{11})_2\text{I}_2$ , is precipitated; this can also be prepared by mixing diamylamine hydriodide and a solution of iodine in hydriodic acid.

On passing methylamine into an ethereal solution of iodine, a black, crystalline *periodide* is precipitated; on adding a solution of iodine in

carbon tetrachloride to a solution of methylamine in the same solvent, methylamine hydriodide is produced, but no additive product.

The non-explosive oil prepared by Guthrie (this Journal, 1863, 16, 239) by adding powdered iodine to a saturated solution of an easily soluble ammonium salt partially decomposed by one-third its equivalent of potassium hydroxide, and by Seamon (Abstr., 1882, 8), by passing ammonia over iodine at  $0^\circ$ , is shown to be similar in all respects to the oil obtained by dissolving nitrogen iodide in ammonium periodide; the mixture dissolves readily in ether, although nitrogen iodide is itself insoluble in ether.

In conclusion, the author states that iodine readily attacks all fatty amines, giving an unstable substitution product and liberating hydrogen iodide, which combines with the amine to form a hydriodide; in aqueous solutions, iodoform appears as an extreme substitution product. An additive compound,  $\text{NR}_3\text{I}_2$ , is only formed in the case of tertiary amines, and even then substitution also takes place. He therefore concludes that nitrogen iodide is not an additive compound,  $\text{NH}_3\text{I}_2$ , as assumed by Chattaway, but a substitution product.

T. M. L.

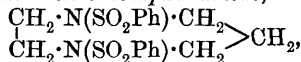
NOTE.—Chattaway has been led by further investigation to the formula  $\text{N}_2\text{H}_3\text{I}_3$  for nitrogen iodide, and regards it as a substitution derivative (Proc., 1899, 17—20).—EDITORS.

**Amines and Amides derived from Aldehydes.** By MARCEL DELÉPINE (*Ann. Chim. Phys.*, 1899, [vii], 16, 103—115; 221—274).—A *résumé* of work already published (compare Abstr., 1898, i, 363, 415, 462; ii, 368, 501, 559; this vol., i, 186, 234, 326, 410, 414), including details of methods of preparation and tables of thermochemical data.

G. T. M.

**Secondary Bases from Ethylenediamine.** By LEOPOLD BLEIER (*Ber.*, 1899, 32, 1825—1830).—By the action of trimethylenic bromide on ethylenediamine, a product, probably a mixture of ethylenediaminehydrobromide and trimethylene-ethylenediaminehydrobromide, was obtained, which could not be further purified.

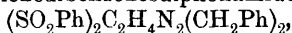
*Trimethylene-ethylenedibenzenesulphonamide,*



obtained by the action of benzenesulphonic chloride (2 mols.) on ethylenediamine (1 mol.) in the presence of an excess of sodium hydroxide solution, crystallises in glistening plates and melts at  $148$ — $149^\circ$ ; when hydrolysed with concentrated hydrochloric acid at  $150$ — $160^\circ$ , it yields *trimethylene-ethylenediamine hydrochloride*,  $\text{C}_2\text{H}_3 \cdot \text{N}_2\text{H}_2 \cdot \text{C}_3\text{H}_6 \cdot 2\text{HCl}$  which crystallises from alcohol in thin, colourless, extremely hygroscopic needles. The *base*,  $\text{C}_5\text{H}_{12}\text{N}_2$ , distils at  $168$ — $170^\circ$ , and then sets to a mass of glistening, colourless crystals; it fumes in the air, is extremely deliquescent, and its aqueous solution has a strongly alkaline reaction; although readily soluble in alcohol or chloroform, the base is only sparingly soluble in ether. The *hydrobromide* crystallises in glistening plates, is extremely hygroscopic, and turns black at  $220^\circ$  without melting; the *platinochloride*,  $\text{C}_5\text{H}_{12}\text{N}_2 \cdot \text{H}_2\text{PtCl}_6$ , crystallises in orange-yellow plates, turns black

at  $270^{\circ}$ , and melts and decomposes at  $292^{\circ}$ . The *aurichloride*,  $C_5H_{12}N_2(HAuCl_4)_2$ , forms a pale, yellow precipitate; the *mercurichloride*,  $C_5H_{12}N_2 \cdot 2HCl \cdot 4HgCl_2$ , is colourless, melts at  $243^{\circ}$ , and is soluble in hot water; the *picrate*,  $C_5H_{12}N_2 \cdot 2C_6H_3N_3O_7$ , crystallises in short, yellow needles which turn black at  $240^{\circ}$  and melt and decompose at  $265^{\circ}$ . The *dinitroso*-derivative,  $C_5H_{10}N_2(NO)_2$ , melts at  $92^{\circ}$ , and is only sparingly soluble in light petroleum; the *dibenzoyl* derivative,  $C_5H_{10}N_2Bz_2$ , crystallises in glistening lamellæ containing water of crystallisation, it loses this at  $103^{\circ}$  and then melts at  $108^{\circ}$ .

Benzylic chloride also reacts with ethylenedibenzenesulphonamide, yielding dibenzylethylenedibenzenesulphonamide,



which crystallises from acetic acid in felted needles melting at  $220^{\circ}$ . When hydrolysed with concentrated hydrochloric acid at  $170$ – $180^{\circ}$ , it yields *dibenzylethylenediamine hydrochloride* which does not melt at  $270^{\circ}$ . *Monobenzylenediamine*,  $C_2H_7N_2 \cdot CH_2Ph$ , may also be obtained by hydrolysing the disulphonamide with concentrated hydrochloric acid; it boils at  $162$ – $165^{\circ}$  under 20 mm. pressure, and rapidly turns yellow on exposure to the atmosphere; its *hydrochloride* crystallises in large, thin plates melting at  $253^{\circ}$ ; the *aurichloride* crystallises in slender needles decomposing above  $230^{\circ}$ ; the *mercurichloride*  $C_2H_7N_2 \cdot CH_2Ph \cdot 2HCl \cdot 2HgCl_2$ , forms small, glistening plates, melting at about  $263^{\circ}$ , and the *picrate*, pale yellow plates or slender needles, melting and decomposing at  $222^{\circ}$ .

J. J. S.

**Occurrence of Acetaldehyde in Petroleum Products.** By CLARENCE J. ROBINSON (*J. Soc. Chem. Ind.*, 1899, 18, 232).—Water which has been in contact with the lighter products from petroleum may contain a small quantity of acetaldehyde. The amount in crude petroleum may be roughly estimated by agitating the sample with water, or, better still, by first distilling off the naphtha and treating this with water; the amount obtained was about 0.001 per cent.

On examining the distillates obtained from crude petroleum, it was found that acetaldehyde is present in the light naphtha first obtained, is practically absent from the heavier products immediately following, and that it again appears and reaches a maximum when the temperature of the still is high enough to produce "cracking." L. DE K.

**Formation of Acetals of Glycol.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 275–277).—The methylene derivative of glycol,  $CH_2 \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array} C_2H_4$ , obtained by Trillat and Cambier (*Abstr.*, 1894, i, 487) by the action of dry trioxymethylene on glycol in presence of a trace of ferric chloride, can be readily prepared by heating a mixture of glycol, 40 per cent. formaldehyde, and syrupy phosphoric acid for a few minutes on the water-bath; on distilling in a current of steam, a product is obtained which boils at  $78^{\circ}$ .

The ethylidene derivative of glycol may be obtained by heating on the water-bath a mixture of glycol and acetaldehyde, in molecular proportion, with syrupy phosphoric acid and a little water; the excess of the aldehyde is dissolved out by means of sodium hydrogen sulphite solution and the liquor rectified.

The *isobutylidene* derivative of glycol,  $\text{CHMe}_2 \cdot \text{CH} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_2\text{H}_4$ , is prepared by heating on a water-bath molecular proportions of glycol and isobutaldehyde with a little water and sufficient syrupy phosphoric acid to give a limpid solution; it is a very mobile liquid, having an unpleasant ethereal odour, boils at  $122\text{--}123^\circ$ , and has a sp. gr. 0.9459 at  $15^\circ$ .

The *methylene* derivative of *monochlorhydrin*,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \cdot \text{CH} \cdot \text{CH}_2\text{Cl} \\ \diagdown \text{O} \cdot \text{CH}_2 \end{array}$ , obtained by distilling a mixture of the monochlorhydrin, 40 per cent. formaldehyde, and phosphoric acid on an oil-bath, is a mobile liquid with an odour resembling that of rum, boils at  $126^\circ$  under 750 mm. pressure, and has a sp. gr. 1.279 at  $0^\circ$ . T. H. P.

**Detection and Isolation of Ketones and Aldehydes.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1806—1807. Compare Bamberger and Kraus, *Abstr.*, 1896, i, 610).—Paranitrophenylhydrazine is strongly recommended as a reagent for aldehydes and ketones, as the hydrazones thus formed crystallise well, and are neither too readily nor too sparingly soluble. Many of the paranitrophenylhydrazones are so markedly acidic that they dissolve in aqueous solutions of alkalis, but many of the alkali salts thus formed are so strongly hydrolysed in aqueous solution, that their characteristic colours only become visible on the addition of alcohol. Extremely dilute aqueous solutions of acetone or of formaldehyde readily react with paranitrophenylhydrazine. *Formaldehydeparanitrophenylhydrazone* crystallises from cold benzene in glistening, yellow needles melting at  $181\text{--}182^\circ$ , and is, in contradistinction to the phenylhydrazone, normally constituted (compare *Abstr.*, 1896, i, 543).

Paranitrophenylhydrazine can be kept for years without decomposition ensuing, whereas the parabromo-compound recommended by Fischer (*Abstr.*, 1892, 439) decomposes when kept for several months. J. J. S.

**Separation of Methyl Ethyl Ketone from Ethylic Alcohol.** By R. DUCHEMIN (*Bull. Soc. Chim.*, 1899, [iii], 21, 314—315).—The use of methyl ethyl ketone for the denaturing of spirits has been suggested by A. and P. Buisine (*Abstr.*, 1898, i, 352), both from the low price and from the difficulty of recovering the alcohol. To 95 per cent. alcohol denatured by the addition of 1/50 of methyl ethyl ketone, the author added quicklime mixed with water and bleaching powder, the whole being kept cool during mixing to prevent the alcohol being attacked. After about 2 hours, the spirit was filtered and rectified in a Le Bel-Henninger tube with three bulbs; 95 per cent. of the alcohol was recovered, and the spirit thus obtained was of good flavour, and had no unpleasant smell. From this it is concluded that the use of methyl ethyl ketone for denaturing spirit is not to be recommended.

The alcohol can also be recovered from spirits mixed with methyl ethyl ketone by the addition of tartaric acid, yielding ethyltartaric acid, which can be crystallised out and purified by pressing between filter papers; on dissolving in water and boiling the solution with potash, almost the whole of the alcohol is obtained free from the ketone.

The ketone can also be destroyed by electrolysis.

T. H. P.

**Condensing Action of Potassium Cyanide on Aldehydes and on Mixtures of Aldehydes and Ketones.** By LUDWIG CLAISEN (*Annalen*, 1899, 306, 322—331. Compare Abstr., 1893, i, 8).—Since the appearance of the author's first communication (*loc. cit.*), the condensing action of potassium cyanide has been investigated by Kohn (this vol., i, 328). Particulars are now given relating to the preparation of aldol, hydracetylacetone, ethylideneacetone, and isobutaldol cyanhydrin. M. O. F.

**A Ketopseudonitrole.** By GIACOMO PONZIO (*J. pr. Chem.*, 1899, [ii], 59, 493—496).—When nitric peroxide (3 mols.) acts on a cold ethereal solution of isonitrosomethyl propyl ketone (4 mols.), crystals of *amylketopseudonitrole*,  $\text{COMe} \cdot \text{CEt} \cdot \text{N}_2\text{O}_3$ , are slowly deposited; it forms unstable, white prisms, melts at  $64^\circ$  to a blue liquid, and decomposes at  $65^\circ$ . It is decomposed on warming or by the continued action of nitric peroxide into methyl ethyl diketone and acetyldinitropropane, and is hydrolysed by dilute potash into acetic and propylnitric acids.

Propylnitric acid forms long, yellowish needles with a sweet taste, melting at  $66^\circ$  (not at  $60^\circ$ ; V. Meyer, Abstr., 1875, 588). R. H. P.

**Preparation of Glycocine.** By VICTOR AUGER (*Bull. Soc. Chim.*, 1899, [iii], 21, 5—7).—An aqueous solution of monochloroacetic acid is saturated with potassium carbonate and mixed with a solution containing slight excess of hexamethylenetetramine; the mixture becomes warm and is evaporated to dryness, preferably in a vacuum. The residue, which consists of the compound  $\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{CH}_2\text{Cl} \cdot \text{COOK}$ , is decomposed by treatment with alcoholic hydrogen chloride; the hydrochloride of ethylic amidoacetate is separated by washing the viscous product with 95 per cent. alcohol, evaporating the filtrate to dryness, treating the residue with calcium carbonate and moist copper oxide, and purifying the copper salt in the usual way. The crude product obtained by extraction may, however, be employed in the preparation of ethylic diazoacetate without further purification. The formal which is also produced by the action of alcoholic hydrochloric acid is reconverted into hexamethylenetetramine by treatment with ammonia. G. T. M.

**Electrolysis of  $\alpha\alpha\beta$ -Trichlorobutyric Acid.** By JULIUS TROEGER and ERICH EWERS (*J. pr. Chem.*, 1899, [ii], 59, 464—469. Compare this vol., i, 12).—Sodium  $\alpha\alpha\beta$ -trichlorobutyrate was electrolysed, using electrodes of spirally rolled platinum foil with an E.M.F. of 16 volts, and a current varying from 0.3 to 0.5 ampère. Carbonic oxide and an unstable oily product were formed at the anode; this oil seemingly has the composition  $\text{C}_2\text{Cl}_4(\text{CHMe} \cdot \text{OH})_2$ , and is probably derived from the action of the sodium hydroxide formed in the electrolysis on the primary product,  $\text{C}_2\text{Cl}_4(\text{CHMeCl})_2$ , of the reaction. R. H. P.

[**Synthesis of Normal Ethereal Salts of Glycerol and Fatty Acids.**] By L. T. C. SCHEIJ (*Rec. Trav. Chim.*, 1899, 18, 169—210).—The normal ethereal salts were prepared by heating, at a temperature in no case exceeding  $200^\circ$ , a mixture of glycerol and the fatty acid in a distilling flask under considerably diminished pressure; a slow

TABLE I.—*Fatty Acids.*

Acid.	Melting point.	Temperature ( $t^{\circ}$ ) at which density and $\mu$ were determined.	Density at $t^{\circ}$ , referred to water at $4^{\circ}$ .	Mol. vol. at $t^{\circ}$ .	$\mu_D$ at $t^{\circ}$ .	Molecular refraction.	Difference for $2CH_2$ .
Butyric .....	-6.5°	20°	0.9590	91.81	1.39906	22.21	$\left. \begin{array}{l} 9.22 \\ 9.33 \\ 9.29 \\ 9.37 \\ 9.35 \\ 9.41 \\ 9.38 \end{array} \right\} \begin{array}{l} \text{Mean for} \\ 2CH_2 = \\ 9.34. \end{array}$
Caproic .....	-8.0	20	0.9274	125.16	1.41635	31.43	
Caprylic .....	16	20	0.9100	158.35	1.42825	40.76	
Caprylic .....	31.1	40	0.8858	194.31	1.42855	50.05	
Capric .....	43.4-43.6	60	0.8642	231.59	1.42665	59.42	
Lauroic .....	53.6	60	0.8584	265.81	1.43075	68.77	
Myristic .....	62.6	80	0.8412	304.56	1.42693	78.18	
Palmitic .....	69.2	80	0.8386	338.92	1.43003	87.56	

TABLE II.—*Ethereal Salts.*

Name.	Melting point.	Density, referred to water at $4^{\circ}$ , at				Mol. vol. at $t^{\circ}$ .		Density at $t^{\circ}$ calculated.	$\mu_D$ at $t^{\circ}$ .	Mol. refraction at $t^{\circ}$ .	
		20°.	40°.	60°.	80°.	$t^{\circ}$ .	Found.	Calculated.		Found.	Calculated.
Tributyryl .....	Below -70°	1.0324	1.0143	0.9963		20°	292.67	294.34	1.43587	76.50	75.98
Tricaproyl * .....	(Between -60° and -25°)	0.9817	0.9651	0.9494		20	393.43	394.39	1.44265	104.24	103.64
Tricapryl * .....	8-8.3	0.9540	0.9382	0.9231		20	492.97	493.96	1.44817	132.01	131.63
Tricapryl * .....	31.1	0.9205	0.9057	0.8904		40	602.26	602.29	1.44461	160.17	159.56
Trilauryl .....	46.4			0.8944		60	713.82	714.40	1.44039	188.27	187.68
Trimyristin .....	56.6			0.8848		80	816.58	817.06	1.44285	216.44	215.73
Tripalmitin .....	65.1				0.8657	60	931.72	933.49	1.43807	244.62	243.99
Tristearin .....	71.6				0.8621	80	1033.12	1036.57	1.43987	272.21	272.13

stream of dry air being kept passing through the mixture in order to remove the water formed, and thus prevent a limit of etherification being reached. By this device, the use of dehydrating agents, which possibly might cause secondary changes, was rendered unnecessary. The glycerol and fatty acids employed were, in all cases, carefully purified; the tables on p. 668 give the physical properties of the substances dealt with. The salts marked with an asterisk in Table II have not been hitherto prepared; the "calculated" values, in the same table, of the molecular refractions and molecular volumes were obtained from the mean values of the same constants for glycerol, water, and the corresponding acid, at the same temperature, as given in Table I. From his values for the melting point of the fatty acids and their glycerides, the author concludes that Berthelot's statement that the normal glyceric salts always melt at a lower temperature than the corresponding acids is not justified. In both tables, the molecular refraction is calculated by the Lorentz-Lorenz formula.

W. A. D.

**Formation of Chains. Ethylic Salts of  $\alpha$ -Bromo-Fatty Acids with (XXXVI) Sodium Methoxide, (XXXVII) Sodium Ethoxide, and (XXXVIII) Sodium Propoxide and Isopropoxide.** By CARL A. BISCHOFF (*Ber.*, 1899, 32, 1748—1755; 1755—1761; 1761—1766. Compare this vol., i, 202, &c.).—The ethylic salt (1 or 2 mols.) was added to the alkyloxide (1 mol.) suspended in light petroleum, and the whole boiled until it became neutral in reaction, for which purpose 20—90 minutes usually sufficed, although in the case of the ethoxide and isovalerate 160 minutes were necessary. (The alkyloxide was usually prepared by evaporating a solution of sodium in the alcohol at 170° under diminished pressure; under these circumstances, however, sodium isopropoxide is largely decomposed into sodium hydroxide and propylene, and so it was prepared by boiling sodium with light petroleum and the calculated amount of the alcohol until all the sodium had disappeared.) The possible products, taking the case of ethylic bromisobutyrate,  $\text{CMe}_2\text{Br}\cdot\text{COOEt}$ , and sodium methoxide as an example, are ethylic methoxyisobutyrate,  $\text{OMe}\cdot\text{CMe}_2\cdot\text{COOEt}$ ; the sodium salts resulting from the hydrolysis of this and the original ethereal salt,  $\text{OMe}\cdot\text{CMe}_2\cdot\text{COONa}$  and  $\text{CMe}_2\text{Br}\cdot\text{COONa}$ ; unsaturated ethylic methacrylate,  $\text{CH}_2\text{:CMe}\cdot\text{COOEt}$ , and its polymeride,  $\text{COOEt}\cdot\text{CMe}\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CMe}\cdot\text{COOEt}$ , and also the sodium salts corresponding with these. The sodium salts and sodium bromide were filtered off, washed with ether, and weighed; the weight of sodium bromide was determined by titration with silver, and that of the sodium salts resulting from hydrolysis by difference. The filtrate was freed from light petroleum and ether, weighed in the crude state, and distilled fractionally, attention being paid to the size of the fractions, which were collected during equal intervals of temperature. Alkyloxysalts and the corresponding unchanged bromo-salts come over at about the same temperature, the unsaturated salts at a lower temperature, and the polymerides at a higher temperature. The ethereal salts experimented with were those of  $\alpha$ -bromopropionic,  $\alpha$ -bromobutyric,

$\alpha$ -bromisobutyric, and  $\alpha$ -bromisovaleric acids, and, in one case, of bromacetic acid also. In nearly all cases, only alkyloxy-salt and unchanged bromo-salt were obtained; the exceptions were those of sodium propoxide with the isobutyrate and isovalerate, when a considerable amount of the unsaturated salt, or of its polymeride, was obtained. The reaction was more rapid with methoxide than with ethoxide; still more so with propoxide; less rapid again with isopropoxide. Of the methoxide, ethoxide, propoxide, and isopropoxide respectively, about 85—95, 73—92, 70—72, and 67—76 per cent. reacted with the bromine of the bromo-salt, the rest acting as a hydrolysing agent; the first amount is fairly constant for the different ethereal salts, except that it is usually lower in the case of the isovalerate. Some experiments were made with sodium ethoxide when this was employed in alcoholic solution instead of suspended in light petroleum; in these, relatively more sodium (94—95 per cent.) reacted with the bromine, and in the case of the isovalerate, unsaturated salt was obtained as well as ethoxy-salt, and the more the higher the temperature at which the reaction was effected.

C. F. B.

**Formation of Chains. Ethylic Salts of  $\alpha$ -Bromo-Fatty Acids with (XXXIX) Sodium Butoxides, (XL) Sodium Isoamyloxyde, Octyloxyde and Isocapryloxyde, and (XLI) Sodium Derivatives of Saturated Monhydric Alcohols.** By CARL A. BISCHOFF (*Ber.*, 1899, 32, 1940—1947; 1948—1953, and 1953—1960. Compare preceding abstract).—The author has quantitatively studied the action of ethylic  $\alpha$ -bromopropionate,  $\alpha$ -bromobutyrate,  $\alpha$ -bromisobutyrate, and  $\alpha$ -bromisovalerate on the sodium derivatives of methylic, ethylic, propylic, butylic, octylic, isopropylic, secondary butylic, isocaprylic,  $\text{CH}_2\text{Me} \cdot [\text{CH}_2]_3 \cdot \text{CHMeOH}$ , isobutylic, isoamylic,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$ , and tertiary butylic alcohols. After boiling equivalent quantities of the bromo-ester and of the sodium alkyloxyde for 1 hour in light petroleum (b. p. 65—70°), the sodium was distributed as sodium bromide, sodium alkyloxyde, sodium salt of the fatty acid, sodium salt of the alkyloxy-acid, or of an unsaturated acid, and each of these was separately determined.

Of the normal alcohols employed, the one with the highest molecular weight, namely, octylic, showed the least condensation with the  $\alpha$ -bromisobutyrate and  $\alpha$ -bromisovalerate. Of the alcohols with single side chains, isopropylic appears to be the least, and isoamylic the most, favourable for the condensation (compare Abstr., 1896, i, 467). The sodium derivative of trimethylcarbinol also gave relatively small amounts of condensation product, especially with ethylic  $\alpha$ -bromopropionate and ethylic  $\alpha$ -bromisobutyrate; with the normal butyrate and isovalerate, it appeared to condense more readily than did sodium isopropoxide. Somewhat remarkable is the fact that sodium isopropoxide, when heated, is decomposed into propylene and sodium oxide, whilst sodium tertiary butoxide under similar conditions is stable.

The constitution of the different alcohols does not appear to affect the condensations mentioned above to nearly the same extent as does the constitution of sodium ethylic malonates, or of aromatic bases previously studied.

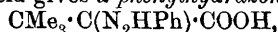


In order to determine whether the increase or contraction of volume on mixing the constituents is an important factor in the condensation, the specific increase or decrease in volume, when the alcohols are mixed with the above-mentioned ethylic salts, was determined. The greatest contractions are given with methylic alcohol, and from propylic alcohol onwards an increase in volume occurs; this increase augmenting in the following order: propylic, butylic, isobutylic, isoamyllic, isopropylic, tertiary butylic, octylic, heptylic, iso-octylic. Of the four ethylic salts employed, the bromobutyrate gives a greater contraction or smaller increase than the bromopropionate, the isobutyrate a smaller contraction or larger increase than the normal butyrate, and the isovalerate a larger contraction or smaller increase than the isobutyrate.

J. J. S.

**Derivatives of Pinacolin.** By E. CARLINFANTI (*Gazzetta*, 1899, 29, i, 269—275. Compare *Abstr.*, 1898, i, 234).—*Ethylic trimethylpyruvate*,  $\text{CMe}_3 \cdot \text{CO} \cdot \text{COOEt}$ , a limpid liquid with a pungent, aromatic odour, distils at  $67-68^\circ$  under 15 mm. pressure, and at  $0^\circ$  has a sp. gr. 0.9716 at  $0^\circ/0^\circ$ , and 0.9583 at  $15^\circ/15^\circ$ . The *phenylhydrazone*,  $\text{CMe}_3 \cdot \text{C}(\text{N}_2\text{HPh}) \cdot \text{COOEt}$ , melts at  $42-43^\circ$ , and crystallises from dilute alcohol in beautiful, white, pearly needles which assume a yellowish tint on exposure to light. By adding the theoretical quantity of concentrated hydrochloric acid drop by drop to a mixture of molecular proportions of the ethylic salt and potassium cyanide kept at  $0^\circ$ , the corresponding *cyanhydrin*,  $\text{CMe}_3 \cdot \text{C}(\text{CN})(\text{OH}) \cdot \text{COOEt}$ , is obtained as a limpid liquid with a faintly nitrilic aromatic odour; it boils at  $119-121^\circ$  under 15 mm. pressure, and has a sp. gr. 1.0462 at  $0^\circ/0^\circ$ . When boiled with a slight excess of 10 per cent. aqueous potash, this cyanhydrin yields the original trimethylpyruvic acid.

Trimethylpyruvic acid gives a *phenylhydrazone*,



melting at  $156-158^\circ$ .

T. H. P.

**Complex Platinum Salts: Oxalates and Nitrites.** By MAURICE VÈZES (*Bull. Soc. Chim.*, 1899, [iii], 21, 143—148. Compare this vol., i, 572). When oxalic acid is added to a hot, concentrated solution of potassium platosonitrite, nitrous fumes are evolved, and the liquid, on cooling, deposits yellow, optically active crystals of *potassium platoso-oxalonitrite*,  $\text{PtC}_2\text{O}_4(\text{NO}_2)_2\text{K}_2 + \text{H}_2\text{O}$ . If a large excess of oxalic acid is used, Söderbaum's platoso-oxalate is formed, and it appears that there is only one salt, the platoso-oxalonitrite, intermediate in composition between the platosonitrite and the platoso-oxalate. The same intermediate salt is produced by the action of potassium nitrite on either modification of potassium platoso-oxalate, by mixing solutions of molecular proportions of potassium platosonitrite and platoso-oxalate, and by the action of normal potassium oxalate on potassium platosodichloronitrite. The converse transformation of the platoso-oxalonitrite into the platosodichloronitrite is easily affected by adding calcium chloride to the solution of the former salt. Similar reactions are found to occur with potassium platosodibromonitrite and platosodi-iodonitrite, the oxalic acid radicle and the halogen being mutually replaceable. N. L.

**Complex Palladium Salts—Pallado-oxalates.** By MAURICE VEZES (*Bull. Soc. Chim.*, 1899, [iii], 21, 172—175. Compare this vol., i, 272 and preceding abstract, also Kane, *Phil. Trans.*, 1842, 132, 297).—*Potassium pallado-oxalate*,  $K_2Pd(C_2O_4)_2 \cdot 3H_2O$ , is obtained when a concentrated solution of potassium oxalate is added to a cold saturated solution of potassium palladochloride,  $K_2PdCl_4$ ; it may also be obtained by the action of potassium oxalate or of oxalic acid on potassium palladonitrite,  $K_2Pd(NO_2)_4$ . It is sparingly soluble in cold, readily in warm, water, and undergoes decomposition when heated at  $80^\circ$ , or when its solutions are boiled. J. J. S.

**Determination of the Molecular Weight of Ethylic Sodiomalonate and Ethylic Sodacetoacetate.** By DANIEL VORLÄNDER and RUDOLF VON SCHILLING (*Ber.*, 1899, 32, 1876—1877).—Determinations of the molecular weight by the boiling point method indicate that neither ethylic sodiomalonate nor ethylic sodacetoacetate undergo dissociation in alcoholic solution into sodium ethoxide and the corresponding ethereal salt; Nef's assumption to the contrary (*Annalen*, 1897, 298, 262) is therefore not justified. The disodium derivatives of ethylic malonate and ethylic acetoacetate do not, however, exist in alcoholic solution. W. A. D.

**Formation of Adipic Acid from the Fraction of Russian Petroleum which Boils at  $80^\circ$  and consists of Naphthenes.** By OSSIAN ASCHAN (*Ber.*, 1899, 32, 1769—1772).—Markownikoff's results (this vol., i, 24) have been confirmed, and his method improved. Some of the lower boiling portion of Baku petroleum, which had not been treated with acid or alkali, was repeatedly fractionated with a fractionating column; from 20 litres of it, about 1.5 litres boiling at  $78$ — $82^\circ$  and with a sp. gr. 0.752 was obtained. This is heated with ten times its weight of nitric acid of sp. gr. 1.42 in a retort with reflux apparatus for 50—60 hours, until the gas that comes off is lighter in colour; the liquid is then evaporated to dryness, the residue digested for 12 hours with an equal volume of cold water, drained and dissolved in 25 per cent. ammonia; the solution is extracted twice with ether, heated to boiling, and acidified with strong hydrochloric acid; the adipic acid which crystallises on cooling is recrystallised from a little boiling water. From 250 grams of the hydrocarbon, 44 grams of the acid were obtained, so that the method is the cheapest and most convenient one for the preparation of adipic acid.

C. F. B.

**Compounds of Certain Organic Acids with Sulphuric Acid.** By SEBASTIAAN HOOGEWERFF and WILLEM A. VAN DORP (*Rec. Trav. Chim.*, 1899, 18, 211—214).—On dissolving certain organic acids in concentrated sulphuric acid, well-defined, crystalline additive compounds separate, which, when exposed to the air, rapidly absorb water and are decomposed. Succinic acid, mesaconic acid, and benzoic acid yield compounds containing 1 mol. of sulphuric acid; the compound obtained from fumaric acid has the composition  $C_4H_4O_4 + 2H_2SO_4$ , and forms beautiful, transparent plates, whilst cinnamic acid yields two derivatives, having the formulæ  $2C_9H_8O_2 + 3H_2SO_4$  and  $C_9H_8O_2 + H_2SO_4$  respectively. W. A. D.

**Action of Ethylic Sodiomalonate on the Dibromides,  $C_nH_{2n}Br_2$ .** By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1899, [ii], 59, 542—556. Compare this vol., i, 481).—By the action of sodium on ethylic malonate and  $\beta$ -diethyltrimethylenic bromide, there is formed a mixture of ethylic ethanetetra-carboxylate and *ethylic diethylallylmalonate*,  $CEt_2 \cdot CH \cdot CH_2 \cdot CH(COOEt)_2$ ; this is an oil boiling at  $161$ — $162^\circ$  under 23 mm. pressure, and of sp. gr.  $1.0017$  at  $0^\circ/0^\circ$ . The acid is an unstable oil, which yields *calcium*, *silver*, and *lead* salts, which are insoluble in water.

*Ethylic methylethylallylmalonate*,  $CMEt \cdot CH \cdot CH_2 \cdot CH(COOEt)_2$ , prepared in similar manner, is a colourless oil boiling at  $155$ — $156^\circ$  under 24 mm. pressure, and of sp. gr.  $1.0037$  at  $0^\circ$ . The acid is an unstable oil, giving insoluble *calcium*, *silver*, and *lead* salts. R. H. P.

**Tautomerism.** By LUDWIG KNORR (*Annalen*, 1899, 306, 332—393. Compare Abstr., 1897, i, 63; 1898, i, 65; and this vol., i, 194).—This paper contains a detailed account of the five isomeric ethylic diacetylsuccinates, a summarised description of which has already appeared.

The author has previously defined a tautomeric compound as a mixture of isomeric substances existing above the stability limit of any single component (Abstr., 1897, i, 66), but he now regards this definition as being too general, and therefore arranges tautomeric substances in two classes; those composed of isomerides capable of mutual interconversion are called *allelotropic* mixtures, pseudomeric compounds being those mixtures in which the conversion can proceed in only one direction. The ethylic diacetylsuccinates and ethylic dibenzoylsuccinates may be regarded as instances of allelotropism, along with the dibenzoylacetylmethanes (Claisen, Abstr., 1896, i, 557), the ethylic mesityloxidoxalates (*loc. cit.*), the tribenzoylmethanes (*loc. cit.*), and the parabromobenzoyldibenzoylmethanes; cases of pseudomerism are to be found in benzoyldiacetylmethane, parabromobenzoylacetone, isocarbopyrotritaric acid (this vol., i, 194), and isophenyl-nitromethane (Hantzsch and Schultze, Abstr., 1896, i, 672).

Solutions of the five isomeric ethylic diacetylsuccinates yield, more rapidly when heated, identical allelotropic mixtures, in which the proportion of enolic to ketonic form depends on the nature of the solvent; this proportion is approximately 1 : 1 in benzene and chloroform, and 3 : 7 in ether and petroleum, appearing to be independent of dilution and temperature. Similar remarks apply to the fused esters at temperatures above  $90^\circ$  (at which the  $\beta$ -modification melts), the proportion of enolic to ketonic form being 3 : 2. The stability limits of the five isomerides appear to coincide with their melting points, and consequently the  $\alpha_1$ -ester cannot be preserved, but slowly becomes crystalline, even when strongly cooled; the spontaneous conversion of the solid  $\alpha_2$ - and  $\gamma$ -modifications into the  $\beta$ -ester is probably due to associated traces of solvent, acting as a catalytic agent. The frequency with which the  $\beta$ -ester is encountered depends on its comparatively high melting point and sparing solubility, and not on relative stability. The conversion of the liquefied enolic esters into the  $\beta$ -ketone proceeds very slowly, but is considerably hastened by the

influence of small quantities of caustic soda, ammonia, or amines; if sodium carbonate is employed, the product contains the second inactive  $\gamma$ -ketone, which is obtained only by this method.

The author's experiences with the three isomeric ethylic dibenzoyl-succinates serve to develop the results obtained with the diacetyl-succinic esters. In the fused and dissolved states, they yield allelotropic mixtures consisting chiefly of the ketones, but identical mixtures are obtained from the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modifications.

It is not possible to do justice in an abstract to the experimental work described in this paper; summaries of the results have already appeared. M. O. F.

**Polyaspartic Acids.** By HUGO SCHIFF (*Gazzetta*, 1899, 29, i, 319—340; and *Annalen*, 1899, 307, 231—246. Compare Abstr., 1898, i, 67; this vol., i, 195).—Although octaspartide unites with 8 mols. of aniline or phenylhydrazine, it only takes up 2 or 3 mols. of ammonia. Octaspartide dissolves in dilute aqueous ammonia, giving a yellow liquid, which, on evaporating, drying, and again treating with aqueous ammonia, gives a yellowish, somewhat crystalline, *ammonium octaspartate*,  $C_{32}H_{34}(NH_4)_8N_8O_{25}$ ; it is a fairly stable salt, and cannot be converted into an amido-compound by heating.

[With GIULIO MARZICHI.]—When octaspartide is acted on by a current of dry ammonia, it turns reddish-yellow, *octaspartotriamide*,  $C_{32}H_{26}N_8O_{17}, 3NH_3$  being formed. This compound loses ammonia, yielding the more stable *octaspartodiamide*,  $C_{32}H_{26}N_8O_{17}, 2NH_3$ , which is slightly soluble in water in the cold, but more so on heating, giving a neutral solution; it is insoluble in benzene, alcohol, chloroform, or carbon bisulphide. The ammonia of the stable diamide is probably combined with the end terms of the octaspartic chain. Whilst 1 molecular proportion of octaspartic acid neutralises 8 equivalents of alkali, the diamide requires in the cold only 3, and on heating 5, equivalents of alkali for its neutralisation. If octaspartodiamide is dissolved in a small quantity of normal potash solution and the liquid just acidified with acetic acid, the addition of copper acetate precipitates a *copper* derivative,  $C_{32}H_{38}Cu_3N_{10}O_{23}$ , with from 16 to 18  $H_2O$ . On decomposing this copper salt with hydrogen sulphide, *diamido-octaspartic acid*,  $C_{32}H_{44}N_{10}O_{23}$ , is obtained; it forms a yellowish, glossy, hygroscopic mass having a strong acid reaction, and readily gives the biuret reaction with potash and copper sulphate.

[With VIERI SEVIERI.]—The removal of the amido-groups from the polyaspartic acids only takes place with great difficulty. When a slight excess of sodium nitrite is gradually added to a cold aqueous solution of octaspartic acid, two of the amido-groups are transformed into hydroxyl groups, giving rise to the nonobasic *dimalohehexaspartic acid*,  $C_{32}H_{26}(NH_2)_6(OH)_2O_{25}$ , which forms a hygroscopic, glassy mass. It gives two greenish-blue basic *copper* salts,  $C_{32}H_{31}Cu_3(CuOH)_3N_6O_{27}$  and  $C_{32}H_{31}Cu_2(CuOH)_5N_6O_{27}$ , and a *lead* salt,  $C_{32}H_{31}Pb_4(PbOH)_4N_6O_{27}$ .

Tetraspartic acid, like the octo-compound, gives up two amido-groups, which, however, are more readily removed. In both cases, the two malic groups produced are at the ends of the polyaspartic chain. Thus tetraspartic acid, on treatment with sodium nitrite,

gives rise to the pentabasic *dimalodiaspartic acid*,  $C_{16}H_{20}N_2O_{15}$ , which forms a normal and a basic *lead* salt of the composition  $Pb(C_{16}H_{15}Pb_2N_2O_{15})_2$  and  $C_{16}H_{15}Pb(PbOH)_3N_2O_{15}$  respectively, and a basic *copper* salt,  $C_{16}H_{15}Cu_2(CuOH)N_2O_{15}$ . T. H. P.

**Chemistry of [Organic Compounds of] Mercury.** By HEINRICH LEY and H. KISSEL (*Ber.*, 1899, 32, 1357—1368).—See this vol., ii, 485.

**Preparation of Ketocumaran and Analogous Compounds.** By PAUL FRIEDLÄNDER (*Ber.*, 1899, 32, 1867—1869. Compare

Abstr., 1897, i, 424).—Ketocumaran (cumaranone),  $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ \text{CO} \end{smallmatrix} CH_2$ , can be prepared by the action of dehydrating agents on phenoxycetic acid, but the yield is very small. When sodium or sodium ethoxide acts on ethyl orthocarboxyphenoxycetate,  $COOEt \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COOEt$ ,

however, *ethylic ketocumancarboxylate*,  $C_6H_4 \begin{smallmatrix} \diagup O \diagdown \\ \text{CO} \end{smallmatrix} CH \cdot COOEt$ , is produced in good yield (compare the synthesis of ethylic indoxylate, Vorländer and Schilling, Abstr., 1898, i, 682); it melts at  $65^\circ$ , dissolves readily in the ordinary solvents, crystallises from dilute alcohol in silky flakes or needles, and can be distilled in a current of steam. The *methylic* salt melts at  $105^\circ$ . The *acid* is unstable, and when distilled in a current of steam, loses carbonic anhydride and is converted into ketocumaran. Other derivatives of ketocumancarboxylic acid can be prepared in a similar manner. T. M. L.

**Synthesis of some Furfuran Derivatives.** By FRANZ FEIST and WILHELM MOLZ (*Ber.*, 1899, 32, 1766—1769).—When a mixture of chloracetone,  $CMeO \cdot CH_2Cl$ , with ethylic acetonedicarboxylate,  $CO(CH_2 \cdot COOEt)_2$ , is treated with ammonia gas in the cold, a product,

$CMe \begin{smallmatrix} \diagup CH \cdot C \cdot COOEt \\ \diagdown NH \end{smallmatrix} \begin{smallmatrix} | \\ C \cdot CH_2 \cdot COOEt \end{smallmatrix}$ , would be expected. In reality but a very little of this is formed; the main product is *ethylic 3-carboxy-2-methyl-furfuran-4-acetate*,  $CH \begin{smallmatrix} \diagup CMe \cdot C \cdot COOEt \\ \diagdown O \end{smallmatrix} \begin{smallmatrix} | \\ C \cdot CH_2 \cdot COOEt \end{smallmatrix}$ ; this boils at  $177-179^\circ$

under 25 mm. pressure; when hydrolysed with an alkali, it yields a mixture of the corresponding dibasic acid and its ethylic hydrogen salt, of which the former is less soluble in ether. *Carboxymethylfurfuran-acetic acid* melts at  $196.5^\circ$ ; when heated, it loses carbonic anhydride, and yields 2:4-dimethylfurfuran-3-carboxylic acid (Abstr., 1893,

i, 403). The *ethylic hydrogen* salt,  $CH \begin{smallmatrix} \diagup CMe \cdot C \cdot COOEt \\ \diagdown O \end{smallmatrix} \begin{smallmatrix} | \\ C \cdot CH_2 \cdot COOH \end{smallmatrix}$ , melts at  $109^\circ$  and forms triclinic crystals [ $a:b:c=0.7112:1:0.7358$ ;  $\alpha=93^\circ 40'$ ,  $\beta=111^\circ 22'$ ,  $\gamma=112^\circ 22'$ ]; when heated, it loses carbonic anhydride and yields an ethylic salt from which 2:4-dimethylfurfuran-3-carboxylic acid is obtained on hydrolysis. C. F. B.

**Ethylene-acetonitrile.** By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 228—232).—The substance obtained on distilling  $\gamma$ -chlorobutyronitrile with powdered caustic potash, which the author considered to

be vinylacetonitrile,  $\text{CN}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$  (this vol., i, 257), is in reality ethylene-acetonitrile [trimethylenecarbonitrile],  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{CN}$ ; it does not combine additively with bromine, and, when hydrolysed yields trimethylenecarboxylic acid,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH}\cdot\text{COOH}$  (Perkin, Trans, 1885, 815; Fittig and Röder, Abstr., 1885, 653).

In conclusion, the author points out that saturated nitriles of the type  $\text{R}\cdot\text{CN}$  boil at approximately the same temperature as the corresponding ethylic salts,  $\text{R}\cdot\text{COOEt}$ . W. A. D.

**Condensation of Ethylic Oxalate with Ethereal Salts of the Glutaric Acid Series.** By W. DIECKMANN (Ber., 1892, 32, 1930—1935).—*Diethylic 2-methyl-4:5-diketopentamethylene-1:3-dicarboxylate*,  $\text{CHMe} < \begin{array}{c} \text{CH}(\text{COOEt})\cdot\text{CO} \\ \text{CH}(\text{COOEt})\cdot\text{CO} \end{array}$ , prepared by boiling ethylic  $\beta$ -methylglutarate (1 mol.) and ethylic oxalate (1 mol.) with sodium ethoxide (2 mols.), separates from alcohol in prismatic crystals and melts at  $108^\circ$ . Orthophenylenediamine converts it into the *phenazine* derivative which crystallises from hot alcohol in yellow needles, melts at  $160$ — $161^\circ$ , dissolves in organic solvents with a greenish-blue fluorescence, and when dissolved in concentrated hydrochloric or sulphuric acid gives the bright red coloration characteristic of quinoxaline derivatives, the colour being destroyed on adding water, but not on adding acetic acid. *Diethylic 2-phenyl-4:5-diketopentamethylene-1:3-dicarboxylate*,  $\text{CHPh} < \begin{array}{c} \text{CH}(\text{COOEt})\cdot\text{CO} \\ \text{CH}(\text{COOEt})\cdot\text{CO} \end{array}$ , is less soluble than the preceding compound, and when crystallised from absolute alcohol melts at  $160$ — $161^\circ$ .

*Diethylic 2:2-dimethyl-4:5-diketopentamethylene-1:3-dicarboxylate*,  $\text{CMe}_2 < \begin{array}{c} \text{CH}(\text{COOEt})\cdot\text{CO} \\ \text{CH}(\text{COOEt})\cdot\text{CO} \end{array}$ , is formed by the action of sodium ethoxide on ethylic  $\beta\beta$ -dimethylglutarate and ethylic oxalate, but the yield is very much smaller than in the case of the monomethyl compound, showing that the second methyl group hinders the condensation; it melts at  $96^\circ$ , and closely resembles the monomethyl compound; a better yield is obtained when the methylic salts are used and the resulting *dimethylic* salt melts at  $117^\circ$ , whilst its *phenazine* derivative crystallises from methylic alcohol in yellow flakes and melts at  $187$ — $188^\circ$ . On reduction, this acid would yield an acid having the formula assigned by Bredt to norcamphoric acid (Marsh and Gardner's camphopyric acid), but this reduction has not yet been accomplished.

T. M. L.

**Chlorination by Means of Ferric Chloride: General Method for the Preparation of Chloriodo-derivatives.** By VICTOR THOMAS (Bull. Soc. Chim., 1899, [iii], 21, 286—288).—The use of ferric chloride as a chlorinating agent can be extended to the preparation of mixed haloid derivatives. Thus, on heating a mixture of ferric chloride and iodobenzene, chloriodobenzene is formed, but secondary reactions also take place, resulting in the liberation of iodine. T. H. P.

**Action of Sodium Ethoxide on Tribromodinitrobenzene.**

By C. LORING JACKSON and WALDEMAR KOCH (*Amer. Chem. J.*, 1899, 21, 510—528).—The process adopted for the preparation of symmetrical tribromodinitrobenzene [ $\text{Br}_3 : (\text{NO}_2)_2 = 1 : 3 : 5 : 2 : 4$ ] is summarised, and a number of products of the action of sodium ethoxide on it are described, in addition to the dinitroresorcinol diethylic ether melting at  $133^\circ$  (Abstr., 1891, 1025), which is now shown to have the structure  $[(\text{OEt})_2 : (\text{NO}_2)_2 = 1 : 3 : 6 : 4]$ .

Tribromodinitrobenzene was dissolved in benzene and heated at  $70^\circ$  for 10 minutes with an alcoholic solution of sodium ethoxide (3 mols.); from the portion soluble in water, no definite product could be isolated, but by extracting the portion insoluble in water with light petroleum, a *bromodinitroresorcinol diethylic ether* was isolated melting at  $92^\circ$  and isomeric with the compound melting at  $184^\circ$ , which forms the chief product when the action takes place in the cold; as the constitution of the latter is proved below, the former compound must have the structure  $[(\text{OEt})_2 : (\text{NO}_2)_2 : \text{Br} = 1 : 3 : 2 : 4 : 5]$ ; it crystallises in bunches of white needles, dissolves readily in cold benzene, ether, chloroform, acetone, acetic acid, carbon bisulphide, ethylic acetate, boiling alcohol, or light petroleum, but is insoluble in water; it becomes brown by long exposure to air, especially in bright light; boiling caustic soda has little or no action on it, but heating with sodium ethoxide converts it almost quantitatively into dinitrophloroglucinol triethylic ether. A small quantity of a *substance* melting at  $112^\circ$  was isolated from the mother liquors; this crystallises from alcohol in white needles and contains bromine, but is not identical with Benedikt's tribromoresorcinol melting at  $110^\circ$ . The portion insoluble in light petroleum consists essentially of the dinitroresorcinol diethylic ether melting at  $133^\circ$ , previously described (*loc. cit.*); when boiled with sulphuric acid of sp. gr. 1.44, it is converted almost quantitatively into symmetrical dinitroresorcinol  $[(\text{OH})_2 : (\text{NO}_2)_2 = 1 : 3 : 6 : 4]$ , which proves its constitution; the dimethylic ether melting at  $167^\circ$  must therefore have a similar structure and not that assigned to it by Beilstein; also the isomeric dimethylic ether melting at  $67^\circ$  can no longer be regarded as having the symmetrical structure assigned to it by Beilstein, since this belongs to the ether melting at  $167^\circ$ . A small quantity of the bromodinitroresorcinol diethylic ether melting at  $184^\circ$  was isolated from the mother liquors, showing that the heating was not sufficiently prolonged to convert it completely into dinitroresorcinol diethylic ether. The chief products of the action are therefore dinitroresorcinol diethylic ether (16 per cent.) and bromodinitroresorcinol diethylic ether melting at  $92^\circ$  (9 per cent.), whilst 75 per cent. of the substance was converted into tarry matter.

When a mixture similar to that used in the previous experiment was allowed to act for three to five days in the cold, a somewhat different series of products was obtained. The aqueous liquors yielded a considerable quantity (6 per cent. of the quantity of tribromodinitrobenzene taken) of a dinitroresorcinol ethylic ether  $[\text{OH} : \text{OEt} : 2\text{NO}_2 = 1 : 3 : 6 : 4]$  melting at  $77^\circ$ , and possibly identical with the compound melting at  $75^\circ$  described by Arönheim (Abstr., 1879, 465), and also gave about 1 per cent. of tribromonitrophenol  $[\text{OH} : \text{NO}_2 : 3\text{Br} =$

1:3:2:4:6] melting at 90°. The portion insoluble in water was extracted with light petroleum, which deposited crystals of dinitro-phloroglucinol triethylic ether melting at 105°; this does not dissolve at all in light petroleum when pure, but a yield of about 19 per cent. of the original substance was obtained from the extract. The mother liquor yielded about 19 per cent. of the bromodinitroresorcinol diethylic ether melting at 92°, which forms the chief product when the action takes place at 70°. The residue insoluble in light petroleum gave a 22 per cent. yield of the bromodinitroresorcinol diethylic ether melting at 184°, and as this is converted by the further action of sodium ethoxide into the dinitroresorcinol diethylic ether melting at 133°, it must have the constitution  $[(\text{OEt})_2 : (\text{NO}_2)_2 : \text{Br} = 1 : 3 : 6 : 4 : 5]$ ; in this case, therefore, the rule holds good that the replacement of a halogen atom by hydrogen only takes place when it is adjacent to two nitro-groups; in the isomeric compound in which the bromine atom is adjacent to only one nitro-group, it is displaced by an ethoxy-group as described above. About 33 per cent. of the original substance remains unaccounted for, and represents the loss incurred in purifying the various products by repeated crystallisation.

The paper also contains a discussion of the 'loosening' influence of the various radicles on one another which renders possible their displacement by the action of sodium ethoxide. T. M. L.

**Action of Acid Solutions of the Lead Salts of Monobasic Fatty Acids on Monochloro- or Monobromo-aromatic Hydrocarbons in which the Halogen is in the Side Chain.** By F. BODROUX (*Bull. Soc. Chim.*, 1899, [iii], 21, 288—291).—The preparation of aromatic ethereal salts, usually carried out by the action of an alcoholic solution of the sodium salt of the acid on halogenated aromatic hydrocarbons having the halogen in the side-chain, is considerably facilitated by using, in place of the sodium salt, the lead salt dissolved in the corresponding acid.

Thus on heating benzylic chloride with an acetic acid solution of lead acetate, lead chloride is precipitated and about 60 per cent. of the theoretical yield of pure benzylic acetate is obtained. Similarly, from lead isobutyrate and benzylic chloride, benzylic isobutyrate is formed and parabromobenzylic bromide and lead acetate yield parabromobenzylic acetate; as the latter is hydrolysed by alcoholic potash, the method gives a ready means of obtaining parabromobenzylic alcohol. Monobromodiphenylmethane and lead acetate react with the production of diphenylmethylic acetate, from which, on hydrolysis, diphenylcarbinol is easily obtained. When monobromotriphenylmethane and lead acetate are heated together, triphenylcarbinol is obtained, the triphenylmethylic acetate suffering decomposition. T. H. P.

**Action of Lead Acetate in Acetic Acid Solution on Benzylidenic Chloride and on Benzotrichloride.** By F. BODROUX (*Bull. Soc. Chim.*, 1899, [iii], 21, 331—333).—The action of lead acetate in acetic acid solution on benzylidenic chloride at the boiling temperature affords a rapid and economical method for preparing benzylidenic acetate. When, however, benzotrichloride is similarly treated, it is



wholly converted into benzoic acid, although it is probable that the triacetate,  $\text{CPh}(\text{OAc})_3$ , is first produced. N. L.

**Glyoxaldiccatechol [Diccatechol Acetylenic Ether].** By CHARLES MOUREU (*Bull. Soc. Chim.*, 1899, [iii], 21, 101—105).—*Glyoxaldiccatechol* [*diccatechol acetylenic ether*],  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{CH} \cdot \text{CH} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{C}_6\text{H}_4$ , formed by the action of acetylenic tetrabromide (1 mol.) on catechol (2 mols.) in the presence of aqueous potash at  $60^\circ$ , crystallises from alcohol in thin scales melting at  $88\text{--}89^\circ$ , and is converted by heating with dilute sulphuric acid into catechol (1 mol.) and a substance of the composition  $\text{C}_8\text{H}_8\text{O}_4$ , which crystallises in white, nacreous scales melting at  $130\text{--}131^\circ$ , is more or less soluble in water and the usual organic solvents, gives an intense blue coloration with ferric chloride, slowly reduces ammoniacal silver nitrate solution in the cold, and forms a *phenylhydrazone* which crystallises in rectangular, white scales melting and decomposing at  $193^\circ$ . It exhibits the characters of a monobasic acid, yields an anhydride crystallising in elongated prisms melting at  $54\text{--}56^\circ$ , and was proved to be identical with Majert's orthohydroxy-phenoxyacetic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ , obtained by the action of chloroacetic acid on catechol (Ger. Pat. 87336 and 87669, 1895). In the formation of this acid by the hydrolysis of diccatechol acetylenic ether, it is suggested that compounds of the composition  $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{CH} \cdot \text{CHO}$  and  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}(\text{OH}) \cdot \text{CHO}$  are intermediate products. N. L.

**Conversion of Hydroresorcinol into Glutaric Acid.** By DANIEL VORLÄNDER and M. KOHLMANN (*Ber.*, 1899, 32, 1878—1879).—Merling has stated (Abstr., 1894, i, 177) that when hydroresorcinol is oxidised with potassium permanganate, glutaric and succinic acids are formed; it is now shown that the oxidation is more easily carried out by using a 10 per cent. solution of an alkaline hypobromite, when glutaric acid is the sole product. Dimethylhydroresorcinol under these conditions gives rise to  $\beta\beta$ -dimethylglutaric acid (compare Komppa, this vol., i, 573), whilst methyl-, phenyl- and furyl-hydroresorcinol yield respectively the corresponding  $\beta$ -glutaric acids. In all cases, small quantities of bromohydroresorcinol are formed during the oxidation; when alkaline hypochlorites are employed, chlorohydroresorcinols are the principal products, little oxidation taking place. W. A. D.

**Action of Chlorine on Homologues of Phloroglucinol.** By MAX SCHNEIDER (*Monatsh.*, 1899, 20, 401—423).—*Pentachlorotriketomethyl-R-hexylene*,  $\text{CO} \begin{smallmatrix} \diagup \text{CMeCl} \diagdown \\ \diagdown \text{CCl}_2 \diagup \end{smallmatrix} \text{CO}$ , prepared by the action of dry chlorine on dry methylphloroglucinol suspended in carbon tetrachloride, crystallises in lustrous plates, melts at  $50^\circ$ , and is very easily soluble in anhydrous ether, benzene, light petroleum, or carbon tetrachloride. *Dichloromethylphloroglucinol*,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \diagup \text{CMe} \diagdown \\ \diagdown \text{CCl} \diagup \end{smallmatrix} \text{C}(\text{OH})$ , obtained by reducing the triketone with stannous chloride or potassium iodide, crystallises from ethylic acetate in small, colourless, lustrous

needles which rapidly become pink on exposure to moist air, melts at  $112-113^{\circ}$ , is very sparingly soluble in water but easily in ethylic acetate, benzene, or alcohol, and crystallises with  $3\text{H}_2\text{O}$ . The *triacetyl* derivative crystallises from alcohol or acetic acid in colourless leaflets, melts at  $166^{\circ}$ , is insoluble in water, easily soluble in warm alcohol, and sparingly so in ether or benzene. By the action of water on pentachlorotriketomethyl-*R*-hexylene, *dichloromethyl  $\alpha$ -chloroethyl ketone* is formed together with dichloroacetic acid; it is a colourless liquid, boils at  $72-74^{\circ}$  under 25–26 mm. pressure, is insoluble in water, but easily soluble in ether, benzene, or light petroleum, and when reduced with sodium amalgam yields a liquid with a sweet alcoholic odour.

By the action of chlorine on moist methylphloroglucinol suspended in carbon tetrachloride, a compound,  $\text{C}_5\text{H}_3\text{Cl}_3\text{O}_2$ , which is probably a tetramethylene derivative,  $\text{CCl}_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CMeCl}$ , is obtained; it crystallises from benzene in colourless, lustrous needles, melts at  $216^{\circ}$ , is insoluble in water, and is decomposed by dilute potassium hydroxide solution.

*Tetrachlorotriketodimethyl-*R*-hexylene*,  $\text{CO} \begin{smallmatrix} \text{CMeCl} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CMeCl} \cdot \text{CO} \end{smallmatrix} \text{CCl}_2$ , prepared by the action of dry chlorine on dimethylphloroglucinol, crystallises from light petroleum in large, colourless plates, has a camphor-like odour, melts at  $44^{\circ}$ , boils at  $149-150^{\circ}$  under 28 mm. pressure, is insoluble in water, easily soluble in light petroleum or benzene, soluble in ethylic acetate or ether, and dissolves in alcohol with partial decomposition. When reduced with stannous chloride, it forms *monochlorodimethylphloroglucinol*,  $\text{OH} \cdot \text{C} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{CCl}$ , which crystallises from chloroform in small, matted needles, is odourless, melts at  $160-161^{\circ}$ , is easily soluble in the ordinary solvents, but almost insoluble in water. The *triacetyl* derivative separates from ethylic acetate or acetic acid in colourless crystals and melts at  $170^{\circ}$ . Tetrachlorotriketodimethyl-*R*-hexylene is much more slowly attacked by water than pentachlorotriketomethyl-*R*-hexylene, and at the ordinary temperature requires several days for any appreciable reaction to occur. When heated with water at  $120-150^{\circ}$ , a strongly acid product with a penetrating odour and a brown, tarry mass is obtained from which no characteristic compounds were isolated.

*Trichlorotriketotrimethyl-*R*-hexylene*,  $\text{CO} \begin{smallmatrix} \text{CMeCl} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CMeCl} \cdot \text{CO} \end{smallmatrix} \text{CMeCl}$ , prepared by the action of dry chlorine on trimethylphloroglucinol, crystallises in colourless, transparent plates, melts at  $49-50^{\circ}$ , boils at  $141^{\circ}$  under 28 mm. pressure, is easily soluble in warm benzene, carbon tetrachloride, chloroform, ether, or light petroleum, and when reduced with stannous chloride yields trimethylphloroglucinol. Trichlorotriketotrimethyl-*R*-hexylene is only partially decomposed by water at  $150^{\circ}$ , forming tarry products with the odour of pyrotartaric acid. The triketone dissolves slowly in dilute potassium hydroxide solution, forming a brownish-yellow solution from which acids liberate carbonic anhydride and precipitate a white sub-

stance which crystallises in leaflets, melts at 142—143°, is soluble in ether, and on remaining in a vacuum over sulphuric acid decomposes into a viscous mass which is insoluble in potassium hydroxide solution. This compound has possibly a lactonic constitution. E. W. W.

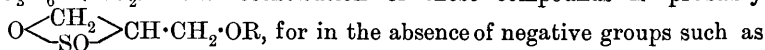
**Nitro-derivatives.** By ANGELO ANGELI (*Gazzetta*, 1899, 29, 275—277).—The author finds that the compound prepared by him by the action of alkali on isosafrole nitrosite (*Abstr.*, 1896, i, 477), to which he gave the formula  $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$ , differs from true nitro-derivatives in not reacting with hydroxylamine. With potash, however, it forms a salt which is decomposed by acetic acid with the precipitation of the original nitro-compound. This behaviour may be explained by supposing the group  $-\text{CH}\cdot\text{C}\cdot\text{NO}_2-$  to change into the isomeric form  $\begin{array}{c} -\text{C}\cdot\text{C}- \\ | \quad | \\ \text{O}\cdot\text{NOH} \end{array}$  T. H. P.

**Action of Sodium Phenoxide on the Dibromo-derivatives of Hydrocarbons.** By WASSILY A. SOLONINA (*Chem. Centr.*, 1899, i, 248—249; from *J. Russ. Chem. Soc.*, 1898, 30, 826—842. Compare this vol., i, 473).—(1)  $\alpha\beta$ -Dibromopropane, when treated with a 25 per cent. solution of sodium phenoxide in alcohol, forms mainly  $\alpha$ -bromopropylene with some  $\beta$ -bromopropylene. (2)  $\alpha\gamma$ -Dibromopropane, under similar conditions, yields phenylic allylic ether,  $\text{PhO}\cdot\text{C}_3\text{H}_5$ , boiling at 188—193° and diphenoxypropane,  $\text{CH}_2(\text{CH}_2\cdot\text{OPh})_2$ , which melts at 61°, whilst from (3)  $\alpha\beta$ -dibromoisobutane,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$ , only  $\alpha$ -bromisobutylene,  $\text{CMe}_2\cdot\text{CHBr}$ , boiling at 89—92° is obtained. (4)  $\beta\gamma$ -Dibromobutane forms  $\beta$ -bromobutylene,  $\text{CMeBr}\cdot\text{CHMe}$ , and a small quantity of an unsaturated substance which is volatile in steam and is probably the compound  $\text{OPh}\cdot\text{CMe}\cdot\text{CHMe}$ . (5) By the action of sodium phenoxide on  $\alpha\delta$ -dibromopentane,  $\alpha$ -phenoxy-3-pentylene,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3\cdot\text{OPh}$ , and  $\alpha\delta$ -diphenoxypentane are obtained. The former is a liquid with a characteristic odour, boils at 226—227°, is volatile in steam, easily soluble in alcohol, ether or benzene, and combines readily with bromine. The latter separates in white crystals, melts at 48—49°, is slightly soluble in cold, easily in hot, alcohol, and in benzene or ether; when heated with hydrobromic acid at 160—170°, it forms the original dibromopentane. (6)  $\alpha\epsilon$ -Dibromohexane yields  $\alpha$ -phenoxy- $\delta$ -hexylene,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$ , and  $\alpha\epsilon$ -diphenoxyhexane. The former is a colourless oil, boils at 243—246°, and is easily soluble in alcohol, ether, or benzene. The latter boils at 225—230° under 20—25 mm. pressure, is easily soluble in alcohol, ether, or benzene, and by the action of hydrobromic acid forms the original dibromohexane. (7) From  $\beta\gamma$ -dibromo- $\beta\gamma$ -dimethylbutane,  $\text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$ , tetramethylethylene,  $\text{CMe}_2\cdot\text{CMe}_2$ , and unsaturated bromo-derivatives, probably containing bromohexylene,  $\text{C}_6\text{H}_{11}\text{Br}$ , are obtained. (8)  $\beta\epsilon$ -Dibromohexane yields mainly  $\beta\epsilon$ -diphenoxyhexane, with a small quantity of  $\beta$ -phenoxy- $\delta$ -hexylene,  $\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OPh}$ . The former crystallises in colourless, monoclinic leaflets (Popoff), melts at 86—86·5°, and when heated with hydrogen bromide forms the original dibromohexane; the latter is a colourless oil, boils at 235—237°, is volatile in steam, and readily unites with bromine. (9)  $\alpha\zeta$ -Dibromo-

hexane reacts quickly with sodium phenoxide, forming  $\alpha\zeta$ -diphenoxy-hexane melting at  $82.5^\circ$ , together with some unsaturated compounds.

From these results, the following conclusions are drawn:—(1) Dibromo-derivatives in which the bromine atoms are in the primary position ( $\text{CH}_2\text{Br}$ ) react with sodium phenoxide to form diphenoxy-derivatives, whilst (2) derivatives containing the bromine atoms united to contiguous carbon atoms in two secondary groups ( $\text{CHBr}$ ), or in a primary and a secondary or in a primary and a tertiary group ( $\text{CBr}$ ), yield only unsaturated bromides. (3) When the bromine atoms are contained in secondary groups separated by several carbon atoms, a mixture of saturated diphenoxy- and unsaturated monophenoxo-derivatives is formed. (4) When both bromine atoms are contained in tertiary groups, only unsaturated hydrocarbons are obtained.

By the action of sulphurous anhydride on the unsaturated monophenylic ethers dissolved in water or in benzene, white, amorphous compounds containing sulphur are formed; these compounds are soluble in alkalis and are decomposed by heat. Thus ethylic allylic ether yields the compound  $\text{C}_5\text{H}_{10}\text{O} + \text{SO}_2$ , methylic allylic ether the compound  $\text{C}_4\text{H}_8\text{O} + \text{SO}_2$ , and allylic alcohol the compound  $\text{C}_3\text{H}_6\text{O} + \text{SO}_2$ . The constitution of these compounds is probably



$\text{COOH}$ ,  $\text{COOR}$ , halogens, &c., only substances which contain the group  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$  are capable of forming such additive products.

E. W. W.

**Dimethylaniline Oxide.** By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, 32, 1882—1903. Compare this vol., i, 347).—When sulphurous anhydride is passed into a dilute aqueous solution of dimethylaniline oxide at  $0^\circ$ , rapid action occurs and a mixture consisting of dimethylaniline (22 per cent.) and its ortho- and para-sulphonic acids (60 and 20 per cent. respectively) is obtained, together with traces of dimethylorthamidophenol and its sulphonic acid; it is probable that the additive compound,  $\text{SO}_3\text{H} \cdot \text{NPhMe}_2 \cdot \text{OH}$ , is first formed, and that subsequent intramolecular rearrangement occurs (compare Abstr., 1897, 286, and 1898, i, 31). The fact that the orthosulphonic acid is obtained as the principal product of this change is of importance, since the direct action of sulphuric acid on dimethylaniline yields the para- and meta-acids exclusively (Evans, *Proc.*, 1896, 234). The formation of dimethylorthamidophenol appears to be due to isomeric change in a portion of the unaltered dimethylaniline oxide, induced by the presence of sulphurous anhydride; it is noteworthy that sulphuric acid is unable to effect this change.

On adding a solution of sodium nitrite (1 mol.) to a solution of dimethylaniline oxide in dilute hydrochloric acid at  $0^\circ$ , a mixture of nearly equal proportions of ortho- and para-nitrodimehtylaniline is obtained, together with traces of paranitrosodimehtylaniline and tetramethylbenzidine. It is probable that in this action the *nitramine*  $\text{OH} \cdot \text{NPhMe}_2 \cdot \text{NO}_2$ , is initially formed, but this could not be isolated owing to its readily undergoing change into the isomeric nitrodimehtyl-

anilines (compare Abstr., 1894, i, 238). Orthonitrodimethylaniline (compare Friedländer, this vol., i, 350) is a mobile, orange-yellow oil which boils at 151—153° under 30—33 mm. pressure, solidifies at  $-20^{\circ}$  to yellowish-red needles, is easily soluble in all organic solvents, and is volatile with steam; the *hydrochloride*,  $C_8H_{10}N_2O_2 \cdot HCl$ , forms snow-white, vitreous needles, and dissociates at 173—174°.

When methylic iodide is left in contact with dimethylaniline oxide dissolved in alcohol, formaldehyde is evolved and a mixture of dimethylaniline, its hydriodide, trimethylphenylammonium iodide and *dimethylaniline oxide sesqui-iodide*,  $(NPhMe_2O)_2I_3$ , obtained; the latter is more readily prepared by adding iodine dissolved in ether to a solution of dimethylaniline oxide in absolute alcohol, and forms reddish-black prisms of a steel-blue lustre which melt and decompose at a temperature between  $99^{\circ}$  and  $101.5^{\circ}$ , depending on the rate of heating; the sesqui-iodide is decomposed on keeping, and when dissolved in caustic soda, gives rise to dimethylaniline oxide. It is probable that the first product of the action of methylic iodide on dimethylaniline oxide is the *compound*  $OMe \cdot NPhMe_2I$ , and that this gives rise to formaldehyde and dimethylaniline hydriodide; the latter is then decomposed by some unchanged dimethylaniline oxide, producing free iodine, which unites with the oxide of the base to form the sesqui-iodide above described.

When aqueous formaldehyde is mixed with a solution of dimethylaniline oxide hydrochloride acidified with dilute sulphuric acid, a solution is obtained which is coloured deep violet-blue on neutralising a portion with soda and adding a mixture of copper and sodium acetate; it is probable that this colour reaction indicates that the *additive* compound,  $OH \cdot NPhMe_2 \cdot CHO$ , is formed initially, but is afterwards decomposed into formic acid and dimethylaniline, along with a small quantity of dimethylorthamidophenol.

Whereas dimethylaniline is characterised by the great activity of the hydrogen atom in the para-position to the  $\cdot NMe_2$  group, especially as regards its power of yielding condensation products, the same atom in dimethylaniline oxide appears to be quite inert; thus, the oxide does not yield azo-compounds by combining with diazo-salts, nor combine with formaldehyde to form an analogue of tetramethyldiamidodiphenylmethane; neither does it seem capable of forming dyes of the indamine or malachite-green type.

W. A. D.

**Orthamidodimethylaniline.** By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, 32, 1903—1907).—*Orthamidodimethylaniline*,  $C_8H_{12}N_2$ , prepared by reducing orthonitrodimethylaniline (preceding abstract) with zinc dust and aqueous ammonium chloride, is a colourless, mobile oil which has a pleasant odour and boils at  $99.5$ — $101^{\circ}$  under 20—25 mm. pressure; on adding ferric chloride to the base suspended in water, a yellowish-brown coloration is produced, which rapidly becomes violet and then blue, and finally, after a long time, deep red; a red coloration is produced immediately on adding ferric chloride to an alcoholic solution of the base. The *benzoyl* derivative,  $NMe_2 \cdot C_6H_4 \cdot NHBz$ , crystallises from dilute methylic alcohol in lustrous needles and melts at  $51^{\circ}$ .

When orthamidodimethylaniline is diazotised and the solution boiled, formaldehyde is evolved and methylaniline formed; it is suggested that the compound  $\text{OMe}\cdot\text{NPhMe}$  is possibly an intermediate product of the action. Traces only of the normal decomposition product, dimethylorthamidophenol, are obtained. W. A. D.

**Preparation of  $\alpha$ -Dinitrodimehtylaniline.** By JOHANNES PINNOW (*Ber.*, 1899, 32, 1666—1669).—Orthonitrodimehtylaniline (which is formed as a bye-product in the preparation of  $\alpha$ -dinitrodimehtylaniline) yields a *picrate* which crystallises in slender, yellow prisms and needles, melts at  $102\text{--}103\cdot5^\circ$ , and dissolves sparingly in acetone and readily in alcohol or ether. *Orthamidodimehtylaniline* is a colourless oil with an odour similar to that of menthol, and boils at  $217\cdot5^\circ$  under 751·5 mm. pressure; it solidifies, when cooled with liquid air, to a glassy mass which melts below  $-50^\circ$ ; the alcoholic solution gives a cherry-red coloration with ferric chloride. The *hydrochloride* dissolves readily in cold water, moderately in hot alcohol, but only slightly in the cold; on adding alcohol to a hot saturated aqueous solution, it separates in white prisms, which soon redden, and melts and decomposes at  $184\text{--}186^\circ$ . The *picrate* crystallises from alcohol in large, yellow, rhomboidal tablets, and melts at  $138\text{--}140^\circ$ . The *acetyl* derivative crystallises from light petroleum in slender, white needles and melts at  $72\text{--}73^\circ$ ; by the further action of acetic anhydride at  $160^\circ$ , it yields 1':2'-dimethylbenzimidazole. T. M. L.

**Derivatives of Aromatic Metadiamines.** By GEORGE F. JAUBERT (*Bull. Soc. Chim.*, 1899, [iii], 21, 18—25).—This paper gives details of the preparation of derivatives of aromatic metadiamines: The following are described for the first time.

*Acetyltrimethylmetaphenylenediamine hydriodide* is obtained in transparent, colourless crystals on heating acetylmetamidodimehtylaniline with methylic iodide and methylic alcohol.

*Nitrosometachlorodimehtylaniline hydrochloride*, produced by treating metachlorodimehtylaniline hydrochloride with sodium nitrite, crystallises from water, alcohol, or acetic acid in golden-yellow needles; when condensed with  $\beta$ -naphthol, it yields a chloro-derivative of Meldola's blue. G. T. M

**Tertiary Aromatic Amines. II.** By CARL HAEUSSERMANN and EUGEN BAUER (*Ber.*, 1899, 32, 1912—1915. Compare this vol., i, 204).—When paradichlorobenzene is heated with potassium and diphenylamine in an atmosphere of hydrogen for 2 hours at  $240\text{--}250^\circ$ , a mixture of two *tetraphenylphenylenediamines* is obtained, together with a large proportion of resin.  $\alpha$ -*Tetraphenylphenylenediamine*,  $\text{C}_{30}\text{H}_{24}\text{N}_2$ , differs from its congener in being sparingly soluble in acetone, from which it crystallises in thin, colourless, lustrous plates which melt at  $199\text{--}200^\circ$ ; on adding a concentrated aqueous solution of sodium nitrite to its solution in glacial acetic acid, the *nitro*-derivative,  $\text{C}_{30}\text{H}_{23}\text{N}_3\text{O}_2$ , separates in vermilion-coloured needles, which, when pure, melt at  $167\text{--}168^\circ$ .  $\beta$ -*Tetraphenylphenylenediamine* is a white, crystalline powder which melts at  $127\text{--}129^\circ$ , and is extremely soluble in acetone and ether, but sparingly in ethylic and methylic alcohols; when treated with sodium nitrite in acetic acid solution, it

yields the *mononitro*-derivative,  $C_{30}H_{23}N_3O_2$ , which crystallises from glacial acetic acid in brownish-yellow, lustrous prisms and melts at  $185-186^\circ$ .

The formation of two tetraphenylphenylenediamines from para-dichlorobenzene is probably due to the latter partially undergoing isomeric change into meta-dichlorobenzene under the conditions of the experiment (compare Istrati, *Abstr.*, 1890, 882); attempts to determine their respective structures have as yet led to no issue.

*Tetraphenylorthophenylenediamine*, prepared from orthodichlorobenzene, separates from alcohol as a microcrystalline powder, melts at  $133-134.5^\circ$ , and dissolves in concentrated sulphuric acid containing a trace of nitrate or nitrite, producing a deep blue coloration.

W. A. D.

**Corrections with Regard to Diazo-compounds.** By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 1717—1721).—The author claims priority for suggesting the formulæ of the diazonium salts,  $R \cdot NCl_2N$ , and of the normal and iso-diazotates,  $R \cdot N:N \cdot OK$ . The statement that the normal diazotates are converted smoothly by the action of benzoic chloride into nitrosobenzanilide, whilst the isodiazotates give only traces of this compound, is incorrect; both compounds give a yield of 50 to 60 per cent. of the nitrosobenzanilide, leaving a residue of 36 to 37 per cent. of normal diazotate; this is explained as being due to the formation of nitrosobenzanilide from both compounds, and the subsequent decomposition of a part of it by the excess of alkali with separation of the normal diazotate. It is also an incorrect statement that the isodiazotates are reduced most readily by sodium amalgam to the hydrazine; both normal and iso-compounds are reduced equally well in presence of an excess of alkali, and the differences which are observed in dilute aqueous solution are due to the partial hydrolysis of the normal diazotates. Similarly, in presence of an excess of alkali, the normal and iso-diazotates behave in exactly the same way on oxidation to phenylnitramine. In the formation of colours from diazo-compounds, the free diazohydrate is the active agent, and the normal diazotates condense most readily by reason of the greater amount of hydrolytic dissociation; in presence of an excess of alkali, no difference is observed. In conclusion, it is stated that the normal and iso-diazotates behave as salts of two very similar acids of different strengths, in accordance with the stereoisomeric forms of the formula,  $Ph \cdot N:N \cdot OK$ , rather than with Bamberger's formulæ,  $PhN(OK):N$ , and  $PhN:N \cdot OK$ .

T. M. L.

**Antidiazohydrates and Primary Nitrosamines.** By ARTHUR HANTZSCH, M. SCHÜMANN, and A. ENGLER (*Ber.*, 1899, 32, 1703—1716; compare this vol., i, 400).—Two groups of substances can be clearly distinguished; (1) true diazohydrates,  $R \cdot N:N \cdot OH$ , electrolytes of acid reaction with definite affinity constants, which combine directly with dry ammonia gas (see note, this vol., i, 401), and interact directly with phosphorus pentachloride and acetic chloride; (2) primary nitrosamines,  $R \cdot NH \cdot NO$ , pseudo-acids which do not conduct, have no effect on indicators, and do not show any definite affinity constant, do not combine directly with ammonia gas, and do not interact with

phosphorus pentachloride and acetic chloride at ordinary temperatures. The primary nitrosamines never yield salts of the formula  $R \cdot NK \cdot NO$ , but always undergo isomeric change and yield true diazotates of the formula  $R \cdot N : N \cdot OK$ .

Thiele's 'nitrosourethane' is a true diazohydrate, and should be called *diazourethane* or *carbethoxydiazohydrate*. Unlike phenylnitrosamine (diazobenzenhydrate), it gives off hydrogen chloride vigorously when treated in ether or benzene solution with phosphorus pentachloride or acetic chloride, even when cooled with a freezing mixture; dry ammonia precipitates the ammonium salt from a solution of the diazohydrate in benzene. Potassium diazourethane (regarded by Thiele as potassium nitrosourethane,  $COOEt \cdot NK \cdot NO$ ) is a neutral salt and very highly dissociated in aqueous solution; at  $0^\circ$ ,  $\mu_{82} = 42.4$ ,  $\mu_{128} = 44.2$ ,  $\mu_{512} = 45.4$ , and  $\mu_{1024} = 45.6$ , whence  $\mu_\infty$  is calculated to be 46 for the potassium salt, and 221 for the free acid. Taking this value of  $\mu_\infty$  for the acid, the conductivity of its aqueous solution at different concentrations gives, for the affinity constant,  $k = 0.00016$  at  $0^\circ$ , that is, free diazourethane at  $0^\circ$  is an acid of about one-tenth the strength of acetic acid, and at  $25^\circ$  would probably be of about equal strength. Lastly, diazourethane can be titrated directly with the calculated quantity of alkali, showing it to be a true acid, and not a pseudo-acid.

Silver diazourethane reacts vigorously with methylic iodide, ethylic iodide, or benzylic iodide. *Methylic diazourethane*,  $COOEt \cdot N : N \cdot OMe$ , is a yellow oil of sharp odour, miscible with organic liquids, but not with water. Unlike the isomeric nitrosomethylurethane, which can be distilled in a current of steam, it is rapidly decomposed by cold water with evolution of nitrogen, and still more rapidly by acids and alkalis. It boils unchanged at  $84^\circ$  under 25 mm. pressure, but is very liable to explode. Zinc dust and acetic acid reduces it to hydrazine.

Thiele's nitrosoguanidine behaves much more like a true nitrosamine; it has a neutral reaction, and when decomposed by acids yields mainly nitrous acid and not nitrogen; it does not interact with phosphorus pentachloride or acetic chloride, and the silver salt is not acted on by methylic iodide.

The so-called 'diazothiazol hydrates' and 'diazouracils' are probably true nitrosamines.

Sodium paranitroantidiazobenzene has a neutral reaction, but appears to be somewhat hydrolysed in very dilute solution. Potassium parabromantidiazobenzene is difficult to obtain free from potassium hydroxide or carbonate, and therefore has an alkaline reaction, but conductivity determinations show that it is not hydrolysed to any large extent. A mixture of this potassium salt with an equivalent quantity of hydrochloric acid had a conductivity in  $N/128$  solution  $\mu = 73.4$  ( $N/128$  KCl gives  $\mu = 73.9$ ) and in  $N/256$  solution  $\mu = 75.0$  ( $N/256$  KCl gives  $\mu = 75.3$ ), showing that the liberated parabromantidiazobenzene hydrate immediately passes into a non-conducting pseudo-acid, namely, the primary nitrosamine,  $C_6H_4Br \cdot NH \cdot NO$ ; the resulting solution was quite neutral and free from nitrous acid. Similar results were obtained with paranitrodiazobenzene hydrate (paranitrophenylnitros-



amine), but owing to its instability the measurements were not so exact. Although the phenomenon of 'gradual neutralisation' cannot be observed, both compounds show 'abnormal neutralisation phenomena' (this vol., i, 400), that is, a neutral solution of the pseudo-acid remains neutral on adding one equivalent of alkali, and, conversely, a neutral solution of a salt remains neutral on adding one equivalent of hydrochloric acid. The nature of the two nitrosamines is also shown by the fact that, unlike diazourethane hydrate, they do not interact with phosphorus pentachloride either in the solid state or in solution, and do not act on acetic chloride when dissolved in benzene or ether, although the solids bring about an evolution of hydrogen chloride; moreover, ammonia gas does not form a salt by direct combination with the solids or with their solutions in benzene, although well-defined salts are produced in dissociating solvents, but, on the other hand,  $\beta$ -naphthol slowly combines with them, both in ethereal and in benzene solution.

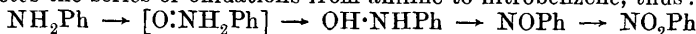
The potassium salt of diazosulphanilic acid is probably a true diazo-compound,  $\text{SO}_3\text{K} \cdot \text{C}_6\text{H}_4\text{N} \cdot \text{N} \cdot \text{OH} + \text{H}_2\text{O}$ , and not a nitrosamine, since (1) it shows an acid reaction in dilute solution, (2) has very little tendency to decompose with separation of nitrous acid, and (3) exhibits an abnormal increase of conductivity in dilute solution, the increment  $\Delta_{1024-64}$  being 8.1 units at  $0^\circ$  as compared with 4.1 for KCl and 4.6 for NaCl, indicating that it is probably comparable to the acid salt of a dibasic acid.

T. M. L.

**Direct Conversion of Aniline into Phenylhydroxylamine.** By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1899, 32, 1675—1678. Compare Caro, *Zeit. angew. Chem.*, 1898, 845).—When aniline is oxidised by a persulphate in presence of ether and in contact with ice, the amount of nitrosobenzene produced is only small, and by extracting the ethereal solution with hydrochloric acid, a solution is obtained which gives all the characteristic reactions of phenylhydroxylamine. In order to separate this from the aniline which is also present, diazobenzene chloride is added, and the phenylhydroxylamine separated in the form of phenylazohydroxyanilide,  $\text{N}_2\text{Ph} \cdot \text{NPh} \cdot \text{OH}$  (*Abstr.*, 1896, i, 222); this crystallises from light petroleum in yellow needles melting at  $126-127^\circ$ , and the alcoholic solution gives a deep blue coloration with a little ferric chloride, and a green coloration on the addition of more ferric chloride; it dissolves in caustic alkalis, forming a yellow salt; chromic acid oxidises it to nitrosobenzene.

*Phenylazohydroxyorthotoluidide*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N}(\text{OH}) \cdot \text{N}_2\text{Ph}$ , prepared in a similar way from orthotoluidine, crystallises in feebly-yellow, silky needles, melts at  $79-79.5^\circ$ , dissolves moderately in alcohol or light petroleum when hot, but only slightly in the cold. The corresponding *para*-compound crystallises from light petroleum in lemon-yellow, silky needles and melts at  $124^\circ$ . Both compounds give the characteristic blue to green coloration on adding ferric chloride to an alcoholic solution.

The direct conversion of aniline into phenylhydroxylamine completes the series of oxidations from aniline to nitrobenzene, thus:



T. M. L.

**Compounds of Phenylhydrazine with Metallic Thiosulphates, Dithionates, and Hypophosphites.** By JOSEPH MOTTESSIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 336—338. Compare Abstr., 1898, i, 132, 133, 413; this vol., i, 205).—*Cadmium thiosulphate phenylhydrazine*,  $\text{CdS}_2\text{O}_3 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ , obtained by mixing solutions of phenylhydrazine, cadmium sulphate, and sodium thiosulphate, crystallises in slender needles which begin to decompose at about  $160^\circ$ , but do not melt below  $250^\circ$ . It is very slightly soluble in cold, more soluble in hot, water or alcohol, and insoluble in ether and chloroform, which, however, gradually decompose it. The corresponding *zinc*, *nickel*, and *cobalt* compounds have been prepared in a similar manner.

*Manganese dithionate phenylhydrazine*,  $\text{MnS}_2\text{O}_6 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ , obtained by adding phenylhydrazine to a 20 per cent. solution of manganese dithionate at about  $80^\circ$ , crystallises in thin, rhomboidal plates and resembles the preceding compound in its behaviour towards solvents. When heated, it begins to decompose at  $125^\circ$ , but does not melt below  $250^\circ$ . The corresponding *zinc* and *cadmium* compounds are obtained by double decomposition.

*Zinc hypophosphite phenylhydrazine*,  $\text{Zn}(\text{PO}_2\text{H}_2)_2 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ , prepared by adding phenylhydrazine to a boiling 15 per cent. solution of zinc hypophosphite, crystallises in rhomboidal plates, and is slightly soluble in cold water and insoluble in cold, slightly soluble in hot, alcohol. The *nickel* salt,  $\text{Ni}(\text{PO}_2\text{H}_2)_2 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ , is formed when phenylhydrazine is added to a cold 10 per cent. solution of nickel hypophosphite and crystallises in greenish-blue, rhomboidal plates. When heated, it becomes yellow at  $170^\circ$ , but does not melt or suffer much decomposition below  $250^\circ$ . It is slightly soluble in cold, and rather more soluble in hot, water, very slightly soluble in alcohol.

Compounds of phenylhydrazine with silver nitrate and with the borates, selenates, and pyrophosphates of the metals of the magnesium group have also been obtained and will shortly be described.

N. L.

**Conversion of Phenylhydrazine into Diazobenzene.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1808).—This conversion is readily brought about by the aid of mercuric acetate, and *α*-naphthylamine may be used as indicator for the diazo-salt which is formed.

J. J. S.

**Paranitrophenylhydrazine Derivatives.** By ELLIS HYDE (*Ber.*, 1899, 32, 1810—1818. Compare this vol., i, 666).—*Paranitrophenylhydrazine picrate*,  $\text{C}_{12}\text{H}_{10}\text{N}_6\text{O}_9$ , crystallises in red needles melting at  $119$ — $120^\circ$ , is insoluble in benzene or light petroleum, but dissolves in hot water, alcohol, or acetone. *β-Formoparanitrophenylhydrazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CHO}$ , crystallises in straw-coloured needles melting at  $182^\circ$ , is readily soluble in the usual solvents, and also in sodium hydroxide solution. The *β*-acetyl compound melts at  $205.5$ — $206^\circ$  (compare Abstr., 1893, i, 534), its *sodium* derivative forms a red powder; the *β*-benzoyl derivative, obtained by the action of benzoic anhydride on the base, crystallises in straw-coloured needles melting at  $193^\circ$ , and is sparingly soluble in benzene, toluene, or hot water.

A *triacetyl* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{Ac})_3$ , may be obtained by the action of acetic anhydride and sodium acetate on the base at  $170-180^\circ$ ; it crystallises in long, colourless, glistening needles melting at  $179-180$ , and dissolves in the usual solvents; when hydrolysed with dilute alkali, it yields the monacetyl derivative described above.  $\beta$ -*Acetodimethylparanitrophenylhydrazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{Me})_2$ , obtained by the action of sodium methoxide and methylic iodide on the monacetyl derivative, crystallises from alcohol in small, yellowish needles melting at  $160-161^\circ$ . All attempts to prepare a monomethyl derivative were unsuccessful.

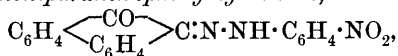
*Paranitrophenylsemicarbazide*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , obtained by the action of potassium cyanate on paranitrophenylhydrazine hydrochloride, crystallises in small, yellowish needles melting and decomposing at  $211-212^\circ$ , and only sparingly soluble in benzene, toluene, or light petroleum.

*Acetaldehyde paranitrophenylhydrazone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{N}(\text{CHMe})_2$ , crystallises in dark, golden-yellow needles melting at  $128.5^\circ$ , and is readily soluble in most solvents, with the exception of light petroleum.

Paranitrophenylhydrazones have been obtained from the following aldehydes and ketones: *Benzaldehyde*—red crystals melting at  $90^\circ$ , and sparingly soluble in sodium hydroxide. *Metanitrobenzaldehyde*—orange-red, glistening plates melting at  $247^\circ$ , and sparingly soluble in most solvents, with the exception of acetone. *Paranitrobenzaldehyde*—flat, reddish-violet, glistening needles melting at  $249^\circ$ . *Acetophenone*—orange-red, glistening needles melting at  $184-185^\circ$ , and readily soluble in most solvents. *Benzophenone*—sulphur-yellow, felted needles melting at  $154-155^\circ$ , and insoluble in aqueous sodium hydroxide. *Cinnamaldehyde*—orange-yellow crystals melting at  $195^\circ$ . *Pyruvic acid*—sulphur-yellow powder melting at  $219-220^\circ$ , and sparingly soluble in benzene, light petroleum, or chloroform.

*Benzilparanitrophenylosazone*,  $\text{C}_2\text{Ph}_2(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , forms a yellow, crystalline powder melting at  $290^\circ$ , and is sparingly soluble in the usual solvents, but dissolves readily in pyridine or nitrobenzene.

*Phenanthraquinoneparanitrophenylhydrazone*,



crystallises from xylene in red needles melting at  $245^\circ$ .

The paranitrophenylosazones of several sugars may be obtained by warming acetic acid solutions of the respective sugars and the base; in most cases, the yield is theoretical. They are best purified by solution in pyridine and precipitation with ether, all have a red colour, and are insoluble in all the usual solvents. Among the products formed in their preparation are always nitrobenzene, paranitraniline, and acetylparanitrophenylhydrazine. The following are the melting points: *glucosazone*,  $257^\circ$  (decomposes); *maltosazone*,  $261^\circ$  (decomposes); *lactosazone*,  $258^\circ$  (decomposes).

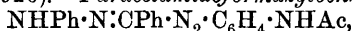
The product obtained by Bamberger and Sternitzky (Abstr., 1893, i, 522) from paranitrophenylhydrazine, acetone, and zinc chloride is 2:4-dichloraniline. The same product is formed when hydrazine sulphate, chloronitrobenzene, and zinc chloride are heated at  $185^\circ$ . Parachloraniline is formed when paranitrophenylhydrazine hydro-

chloride is heated with concentrated hydrochloric acid at 200°, whilst with dilute hydrochloric acid (1:1) at 120—130° the products are nitrobenzene, paranitraniline, and the unaltered base. J. J. S.

**Action of Phenylhydrazine on Chloranilic Acid.** By HENRI IMBERT and A. DESCOMPS (*Bull. Soc. Chim.*, 1899, [iii], 21, 72—74).—When chloranilic acid and phenylhydrazine react in absolute alcoholic solution, a *compound* is obtained isomeric with that produced when 80 per cent. alcohol is employed (this vol., i, 205). The new substance is colourless, and may be converted into the brown isomeride by treating it with 90 per cent. alcohol, but the inverse change has not been effected. G. T. M.

**Action of Hydrazines on Chloranilic and Bromanilic Acids.** By A. DESCOMPS (*Bull. Soc. Chim.*, 1899, [iii], 21, 366—368).—Bromanilic acid resembles chloranilic acid (this vol., i, 205) in reacting with phenylhydrazine in alcoholic solution to form a *compound*,  $C_6Br_2O_2(OH)_2 \cdot 2N_2H_3Ph$ , which crystallises in red needles, and is converted by the action of 90 per cent. alcohol into a brownish-violet isomeride. The action of hydrazine hydrate on bromanilic acid, however the conditions may be varied, leads to the formation of only *one* compound, a brick-red, crystalline *substance* of the composition  $C_6Br_2O_2(OH)_2 \cdot 2N_2H_4$ . The same applies to the action of hydrazine hydrate on chloranilic acid. N. L.

**Paracetamidoformazylbenzene.** By EDGAR WEDEKIND (*Ber.*, 1899, 32, 1918—1920).—*Paracetamidoformazylbenzene*,



prepared by the action of paracetamidodiazonium chloride on benzaldehydephenylhydrazone, is a reddish-black, crystalline powder, which melts at 212—213° and dissolves readily in acetone or acetic acid. Attempts to remove the acetyl group by hydrolysing with acids or alkalis gave no definite results. When suspended in alcoholic hydrogen chloride, it is readily oxidised by nitrous anhydride, the colour changing from red to yellowish-brown; on diluting with water and adding potassium iodide, *paracetamidotriphenyltetrazolium iodide*,

$C_6H_5 \cdot C \begin{smallmatrix} \swarrow N \cdot NPh \\ \searrow N : NI \cdot C_6H_4 \cdot NHAc \end{smallmatrix}$  is thrown down as a yellow precipitate, which, when crystallised from hot water, melts at 289°; alkaline reducing agents convert it into the original formazyl-compound.

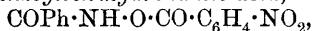
The *α-metanitrophenylhydrazone* of *ethyl αβ-diketobutyrate*,  $CH_3 \cdot CO \cdot C(COOEt) : N_2H \cdot C_6H_4 \cdot NO_2$ , crystallises from hot dilute alcohol and melts at 129—131°; the free *acid* is canary-yellow, melts between 170° and 175°, and gives an orange-yellow precipitate with phenylhydrazine. T. M. L.

**Isomeric Change in the Benzhydroxamic Acid Group.** By ALFRED WERNER and W. SKIBA (*Ber.*, 1899, 32, 1654—1666. Compare Abstr., 1894, i, 585).—By the action of silver metachlorobenzoate on benzhydroximic chloride, a small amount of benzildioxime peroxide,  $N \begin{smallmatrix} \swarrow CPh \cdot CPh \\ \searrow O \end{smallmatrix} N$ , is produced, the chief product being *metachloro-*

*benzoylbenzhydroxamic acid*,  $\text{OH} \cdot \text{CPh} \cdot \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl}$  or  
 $\text{COPh} \cdot \text{NH} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl}$ ;

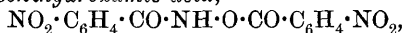
this separates from alcohol in prismatic crystals, melts at  $156^\circ$ , and is also prepared synthetically from benzhydroxamic acid and meta-chlorobenzoic chloride. The intermediate product is probably meta-chlorobenzoylbenzhydroxamic acid,  $\text{NOH} \cdot \text{CPh} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Cl}$ , but this could not be isolated, as it immediately changes in the normal manner into the isomeric hydroxamic acid on the one hand and into benzildioxime peroxide and metachlorobenzoic acid on the other.

The action of silver metanitrobenzoate on benzhydroxamic chloride gives benzildioxime peroxide and metanitrobenzoic acid, but the chief product is *metanitrobenzoylbenzhydroxamic acid*,



which crystallises from benzene, melts at  $151^\circ$ , and is also prepared from benzhydroxamic acid and metanitrobenzoic chloride; the intermediate hydroxamic acid could not be isolated. *Paranitrobenzoylbenzhydroxamic acid* separates from methylic alcohol in glistening crystals, and melts at  $172^\circ$ , whilst *orthonitrobenzoylbenzhydroxamic acid* melts at  $131$ – $132^\circ$ ; these were obtained in the same way as the metanitro-acid, but in the case of the paranitro-compound the benzildioxime peroxide forms the principal product of the reaction.

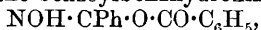
The chief products of the action of silver metanitrobenzoate on metanitrobenzhydroxamic chloride are metanitrobenzoic acid and metanitrobenzildioxime peroxide, melting at  $182$ – $184^\circ$ ; *metanitrobenzoylmetanitrobenzhydroxamic acid*,



is also produced in smaller quantity; it melts at  $153$ – $156^\circ$ , and is also prepared by the action of metanitrobenzoic chloride on metanitrobenzhydroxamic acid; the intermediate hydroxamic acid could not be isolated. *Metanitrobenzhydroxamic acid* crystallises from alcohol and melts at  $151^\circ$ . The interaction of silver benzoate and metanitrobenzhydroxamic chloride gives metadinitrobenzildioxime peroxide and benzoic acid as the chief products, together with a small amount of *benzoylmetanitrobenzhydroxamic acid* which melts at  $153^\circ$ , and is prepared synthetically from benzoic chloride and metanitrobenzhydroxamic acid.

The interaction of silver paranitrobenzoate and paranitrobenzhydroxamic chloride gives only paradinitrobenzildioxime peroxide and paranitrobenzoic acid. *Paranitrobenzhydroxamic acid* crystallises from alcohol and melts at  $177^\circ$ ; *paranitrobenzoylparanitrobenzhydroxamic acid* crystallises from alcohol in glistening needles and melts at  $173$ – $176^\circ$ . The action of silver benzoate on paranitrobenzhydroxamic chloride gives paranitrobenzildioxime peroxide and benzoic acid as the only products. *Benzoylparanitrobenzhydroxamic acid* crystallises from alcohol in fine, colourless flakes and melts at  $178^\circ$ .

It will be seen that the benzoylbenzhydroxamic acid,



isolated as the first product of the interaction of silver benzoate and benzhydroxamic chloride (*loc. cit.*), becomes unstable on the introduction of a chlorine atom or a nitro-group into either benzene nucleus. Benzoylbenzhydroxamic acid passes almost completely into

the isomeric hydroxamic acid and only a small quantity breaks down into benzildioxime peroxide and benzoic acid; in the interaction of a substituted silver benzoate on benzhydroximic chloride, however, the proportion of the dioxime peroxide is materially increased, and it becomes the chief product when metanitrobenzhydroximic chloride is used, and the only product in the case of paranitrobenzhydroximic chloride.

T. M. L.

**Action of Zinc Ethyl on the so-called Nitramines and Isonitramines.** By ARTHUR HANTZSCH (*Ber.*, 1899, 32, 1722—1723).—On mixing ethereal solutions of zinc ethyl and phenylnitramine, the additive compound,  $\text{PhN}_2\text{O}_2\text{H} + 4\text{ZnEt}_2$ , is precipitated as a white, crystalline substance, fairly stable in air but decomposed on acidifying and extracting with ether, when the original nitramine is recovered. Phenylisonitramine (nitrosophenylhydroxylamine) gives an additive compound,  $\text{PhN}_2\text{O}_2\text{H} + 2\text{ZnEt}_2$ , which is also decomposed by dilute acids, giving rise to the original nitramine. Benzylisonitramine also gives an additive compound with zinc ethyl, but the isomeric benzylic ethers derived from it as well as methylic phenylisonitramine are not acted on. These results are taken as indicating that the so-called nitramines, like the isonitramines, are probably hydroxylic compounds, and not true nitramines.

With reference to Lachman's statement (this vol., i, 326), the author never questioned the existence of triethylamine oxide, but merely the fact of its boiling without decomposition.

T. M. L.

**Symmetrical Dinitrodiphenylcarbamides.** By HENRI VITENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 148—158).—*Diparanitrodiphenylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , prepared by heating phenylic carbonate (1 mol.) with paranitraniline (2 mols.) for 3 hours at  $200^\circ$ , crystallises from boiling alcohol in yellow, silky needles, and sublimes at about  $310^\circ$  without melting; it is insoluble in water, benzene, chloroform, acetone, or ether, slightly soluble in boiling alcohol, more soluble in boiling nitrobenzene. When reduced with tin and hydrochloric acid, it yields a stannic derivative which is converted by treatment with hydrogen sulphide into the hydrochloride of diparamidodiphenylcarbamide,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , from which the base is liberated by ammonia. Fleischer and Nemes (this Jour., 1877, ii, 886) prepared this base by reducing the tetranitrodiphenylcarbamide, obtained by the nitration of diphenylcarbamide, and since paraphenylenediamine was found to be simultaneously produced they inferred the formation of tetranitroazoxybenzene in the nitration of diphenylcarbamide. This hypothesis is now shown to be unfounded, since paraphenylenediamine is also produced in the reduction of the pure dinitrodiphenylcarbamide prepared in the manner described above.

Dimetanitrodiphenylcarbamide has been obtained by several observers, but the melting points assigned to it have varied greatly. As obtained by the action of phenylic carbonate on metanitraniline, it crystallises either in white needles or in yellow plates, the former modification changing into the latter when heated at  $190^\circ$ , and finally melting sharply at  $242^\circ$ . Both modifications, when reduced with tin and hydrochloric acid, yield one and the same stannochloride,

$C_{13}H_{14}N_4O, 2HCl, 2SnCl_2 + 2\frac{1}{2}H_2O$ , which crystallises in long, white, silky needles, and is converted by treatment with hydrogen sulphide into *dimetamidodiphenylcarbamide*, which crystallises in small, white needles melting at  $208-209^\circ$ . The isomerism observed with dimetanitrodiphenylcarbamide does not therefore extend to its derivatives.

*Diorthonitrodiphenylcarbamide*,  $CO(NH \cdot C_6H_4 \cdot NO_2)_2$ , could not be prepared by the action of phenylic carbonate on orthonitraniline, but was readily obtained by heating orthonitraniline with carbonyl chloride in a sealed tube at  $130^\circ$ ; it forms yellow crystals melting at  $225^\circ$ , and yields a stannochloride which is converted by the action of hydrogen sulphide into *diorthamidodiphenylcarbamide*, which crystallises in slender, white needles melting and subliming at  $243-245^\circ$ .

N. L.

**Symmetrical Chloro-, Bromo-, and Iodo-diphenylcarbamides.** By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 302-306).—These compounds can be obtained by heating the corresponding halogenated anilines (2 mols.) with phenylic carbonate.

*Paradichlorodiphenylcarbamide*, prepared by heating parachloraniline (2 mols.) with phenylic carbonate (1 mol.) for two hours at  $200^\circ$ , forms white needles, melts and sublimes at  $306-307^\circ$ , and is readily soluble in boiling glacial acetic acid, less so in boiling alcohol, and insoluble in water, ether, benzene, or chloroform.

*Metadichlorodiphenylcarbamide*,  $CO(NH \cdot C_6H_4Cl)_2$ , crystallises in small, white needles melting at  $245^\circ$ , and dissolves in hot glacial acetic acid or alcohol, and to a slight extent in cold alcohol, but is insoluble in water, ether, benzene, or chloroform.

*Orthodichlorodiphenylcarbamide* forms small, white needles melting at  $235-236^\circ$ , and is insoluble in water, benzene, ether, or chloroform, but is dissolved by hot alcohol or glacial acetic acid.

*Paradibromodiphenylcarbamide* forms thin, white plates which, on heating, do not melt, but sublime unchanged at  $330^\circ$ .

*Metadibromodiphenylcarbamide* forms white needles melting at  $263^\circ$ , and dissolves in hot alcohol or glacial acetic acid, but is insoluble in water and the neutral organic solvents.

*Orthodibromodiphenylcarbamide* crystallises in small, white needles which melt at  $219-220^\circ$ , and is soluble in hot alcohol or acetic acid, but insoluble in water, benzene, or chloroform.

These carbamide derivatives can also be obtained by the action of phosgene on haloid derivatives of aniline. *Paradi-iododiphenylcarbamide*,  $CO(NH \cdot C_6H_4I)_2$ , so obtained, forms thin, white needles which sublime without melting at above  $300^\circ$ , and is insoluble in all the ordinary organic solvents except boiling glacial acetic acid, which dissolves it only slightly; it does not lose its iodine even when boiled with concentrated nitric or nitrohydrochloric acid, but on calcining it with excess of quicklime, the iodine is removed. This compound can not be obtained by heating pariodaniline with phenylic carbonate, as decomposition takes place with the formation of a tarry mass and the liberation of large quantities of iodine.

T. H. P.

**Chlorination of Hydrobenzamide.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 10-11).—By the chlorination of hydro-

benzamide, Müller, in 1859, obtained a viscid oil which had the composition  $C_{21}H_{18}N_2Cl_4$ ; this substance, on heating at  $180-220^\circ$ , evolved hydrogen chloride and yielded a liquid boiling at  $187^\circ$  which had a composition corresponding with  $C_{21}H_{17}ClN_2$ . The author finds that this product is in reality a mixture of benzonitrile (2 mols.) and benzylic chloride (1 mol.), the former constituent being separated and identified by its compound with hexamethylenetetramine, and the latter by hydrolysis to benzoic acid. The viscid oil is an additive compound whose constitution may be represented by the formula  $CHPhCl \cdot NCl \cdot CHPh \cdot N : CHPh$ . G. T. M.

**Synthesis of Aromatic Thioanilides.** By LUDWIG GATTERMANN [and in part FRIEDMANN, KNÜTTEL, VON KÜYLENSTJERNA, J. A. RÖLÖFSEN, F. SCHAAR-ROSENBERG, TETZLAFF, TUST, and ZIMMER] (*J. pr. Chem.*, 1899, ii, 59, 572—594).—Thiocarbimides condense with aromatic hydrocarbons and phenolic ethers in the presence of aluminium chloride to form aromatic thioanilides. The reaction takes place in two stages. Hydrogen chloride which is always present when aluminium chloride is used, combines with the thiocarbimide, forming the unstable chloride of a thiocarbamic acid, which then reacts with the hydrocarbon or phenolic ether to form the thioanilide. The thioanilides are well characterised substances, but are only hydrolysed with difficulty, heating in a sealed tube to  $180^\circ$  with dilute sodium carbonate for five hours being recommended as the best method.

The following rules hold in this synthesis, (I) with homologues of benzene the  $-CS \cdot NPh$  group takes up a para-position to an alkyl group. (II) Similarly, phenolic ethers give parathioanilides. (III) With homologues of phenolic ethers, it is the ether group, and not the alkyl group, which determines the position of the  $-CS \cdot NPh$  group. (IV) If the para-position to the ether group in a phenolic ether is occupied by an alkyl group, the  $-CS \cdot NPh$  group takes up the ortho-position. In general, on treating the thioanilides with iodine in alcoholic solution, the sulphur is replaced by oxygen.

On oxidation with potassium ferricyanide, the thioanilides give ring compounds of the type  $CPh \begin{smallmatrix} S \\ \diagdown \diagup \\ N \end{smallmatrix} C_6H_4$ . Benzene and phenylthiocarbimide give a poor yield of thiobenzanilide; by the action of aluminium chloride on the phenylthiocarbimide, a secondary product melting at  $154^\circ$  is obtained, which is identical with that obtained by the action of bromine on the phenylthiocarbimide (Proskauer and Sell, *Abstr.*, 1877, i, 67).

Phenylthiocarbimide and toluene give *thioparatoluanilide*, which forms long, bright yellow needles, melts at  $140-141^\circ$ , and yields paratoluic acid on hydrolysis. The *thioanilide* from orthoxylene and phenylthiocarbimide forms yellow prisms, melts at  $106-107^\circ$ , and gives 3:4-dimethylbenzoic acid on hydrolysis. In similar manner, metaxylene gives 2:4-dimethylthiobenzanilide, crystallising from alcohol in the form of pale yellow prisms melting at  $106.5-107.5^\circ$ . Toluene and tolylthiocarbimide yield the *paratoluidide* of *parathiotoluic acid*, which forms large, yellow crystals melting at  $165-166^\circ$ ; this on hydrolysis gives paratoluic acid, and on treatment with iodine, paratoluic para-



toluidide. As a bye-product, the sulphide of paratolylthiocarbimide is obtained, which crystallises from glacial acetic acid in the form of bright yellow needles melting at 183—184°.

Anisoil and phenylthiocarbimide yield *paramethoxythiobenzanilide*, which crystallises in long, bright yellow needles, and melts at 153—154°; on oxidation, this yields colourless needles melting at 134—135°. Phenetoil and phenylthiocarbimide yield *paraphenoxy-4-thiobenzanilide*, which forms long, bright yellow needles melting at 143°; the product obtained from it by oxidation forms colourless leaflets melting at 120°. Orthotolylic methylic ether and phenylthiocarbimide give *paramethoxymetamethylthiobenzanilide*, crystallising in yellow needles and melting at 177°. *Parethoxymetamethylthiobenzanilide* forms long, yellow needles and melts at 169°, and the corresponding *parethoxymetamethylbenzoic acid*, obtained by its hydrolysis, forms colourless needles melting at 199°.

*Paramethoxyorthomethylthiobenzanilide* forms yellow needles melting at 96°. *Parethoxyorthomethylthiobenzanilide* crystallises in yellow needles melting at 117°, and *parethoxyorthomethylbenzoic acid*, obtained by its hydrolysis, crystallises from water in colourless needles melting at 146°.

Parethoxytoluene and phenylthiocarbimide yield *4-ethoxy-5-methylthiobenzanilide*, which crystallises in yellow needles melting at 111°.

Thymylic methylic ether and phenylthiocarbimide yield *4-methoxy-2-methyl-5-isopropylthiobenzanilide*, which forms yellow, prismatic crystals and melts at 132—133°. *4-Ethoxy-2-methyl-5-isopropylthiobenzanilide*, forms yellow prisms and melts at 147—148°.

With phenylthiocarbimide, resorcinol diethylic ether yields *2:4-diethoxythiobenzanilide*, which crystallises in yellow needles and melts at 121°; diphenylic ether yields *paraphenoxythiobenzanilide*, which forms yellow scales melting at 133°.

Phenylthiocarbimide, with 1-methoxynaphthalene, gives a thioanilide crystallising from glacial acetic acid in the form of yellow prisms melting at 179°; with 1-ethoxynaphthalene, a thioanilide in the form of yellow needles from glacial acetic acid melting at 199—200°; with 2-methoxynaphthalene and 2-ethoxynaphthalene, thioanilides crystallising from alcohol in the form of flat, yellow crystals melting respectively at 141° and 164—165°. Attempts to hydrolyse these compounds were unsuccessful, and their constitution is doubtful.

Phenylthiocarbimide gives with orthochlor-, brom-, and iod-anisoil respectively, *3-chloro-4-methoxythiobenzanilide*, which forms yellow plates melting at 205°, *3-bromo-4-methoxythiobenzanilide*, which crystallises in flat, yellow needles melting at 204°, and *3-iodo-4-methoxythiobenzanilide*, which forms yellow needles melting at 206·5°; with orthochlorophenetoil, *3-chloro-4-ethoxy-thiobenzanilide*, which forms broad, yellow needles melting at 195·5° is obtained.

Diphenylic ethylenic ether and phenylthiocarbimide give a thioanilide of the formula  $C_2H_4(O \cdot C_6H_4 \cdot CS \cdot NHPh)_2$ , forming lustrous, yellow plates and melting at 255°.

Orthotolylthiocarbimide yields, with anisoil, *paramethoxythiobenzorthotoluidide*, which forms yellow needles melting at 95°; with phenetoil, *parethoxythiobenzorthotoluidide* is obtained in yellow needles melting at 106°; with orthotolylic ethylic ether, *4-ethoxy-3-methylthiobenzorthotoluidide* is obtained as yellow needles melting at 137°.

Metatolylthiocarbimide yields, with anisoil, *paramethoxythiobenzo-metatoluidide*, which crystallises in yellow needles melting at 125°; with phenetol, *parethoxythiobenzo-metatoluidide* is obtained as yellow needles melting at 130°.

Paratolylthiocarbimide gives, with anisoil, *paramethoxythiobenzo-paratoluidide*, which forms yellow needles melting at 157°; with phenetol, *parethoxythiobenzo-paratoluidide* is obtained; it forms yellow needles melting at 151°; with orthotolylic ethylic ether, *4-ethoxy-3-methylthiobenzo-paratoluidide* is obtained, crystallising in yellow needles and melting at 185°.

Metaxylylthiocarbimide gives, with phenetol, *parethoxythiobenzo-metaxylylidide*, which forms flat, yellow crystals melting at 139—140°; with orthotolylic ethylic ether, *4-ethoxy-3-methylthiobenzo-metaxylylidide* is obtained as yellow needles melting at 132—133°.

Pseudocumylthiocarbimide (? which), with orthotolylic ethylic ether, gives a thioanilide of the formula  $\text{OEt} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_2\text{Me}_2$  [1 : 2 : 4], which forms yellow needles melting at 143°.

Paranisylthiocarbimide gives, with anisoil, *paramethoxythiobenzo-paranisidide*, which forms small, yellow needles melting at 148°; with phenetol, *parethoxythiobenzo-paranisidide* is obtained, crystallising in long, yellow needles melting at 154·5°.

*Paraphenetylthiocarbimide*, prepared from paraphenetidine and thiophosgene, forms colourless leaflets melting at 62·5°; with anisoil, it yields *paramethoxythiobenzo-paraphenetidide*, which forms yellow needles melting at 135·5°; with phenetol, it yields *parethoxythiobenzo-paraphenetidide*, which crystallises in small, yellow needles melting at 151—152°, and, with iodine, gives *parethoxybenzo-paraphenetidide*, forming colourless needles melting at 171°, and with potassium ferri-cyanide, a colourless oxidation product melting at 163°.

*Parachlorophenylthiocarbimide*, with anisoil, gives *paramethoxythiobenzo-parachloranilide*, which forms thick, yellow prisms melting at 182°; with phenetol, *parethoxythiobenzo-parachloranilide* is formed, crystallising in thick, yellow prisms melting at 194—195°; with orthotolylic ethylic ether, *4-ethoxy-3-methylthiobenzo-parachloranilide* is obtained as yellow prisms melting at 203°; with  $\alpha$ -naphthyllic methylic ether, *4-methoxythionaphtho-parachloranilide* is obtained, crystallising in bright yellow prisms melting at 205—206°; the corresponding *ethoxy*-compound forms small needles melting at 191—192°.

*Metabromophenylthiocarbimide*, prepared by adding metabromaniline to thiophosgene in chloroform solution, boils at 256°; with anisoil, it yields *paramethoxythiobenzo-metabromanilide*, which forms yellow needles melting at 150—151°; with phenetol, the corresponding *ethoxy*-compound, melting at 139°, is obtained; with orthotolylic ethylic ether, *4-ethoxy-3-methylthiobenzo-metabromanilide* is formed, crystallising in yellow needles and melting at 144°; with  $\alpha$ -naphthyllic methylic ether, *4-methoxythionaphtho-metabromanilide* is obtained, crystallising in yellow needles and melting at 149—150°; the corresponding *ethoxy*-compound melts at 159—160°.

$\alpha$ -Naphthylthiocarbimide, with anisoil, gives *paramethoxythiobenzo- $\alpha$ -naphthalide*, which forms deep yellow prisms melting at 147—148°; the corresponding *ethoxy*-compound forms yellow prisms melting at 156—157°; with orthotolylic ethylic ether, it gives *4-ethoxy-3-methyl-*

*thiobenzo- $\alpha$ -naphthalide*, which forms yellow needles and melts at  $154-155^{\circ}$ ; with  $\alpha$ -naphthyl methylic ether, it gives *4-methoxythio- $\alpha$ -naphtho- $\alpha$ -naphthalide*, crystallising in bright, yellow needles and melting at  $196-197^{\circ}$ ; the *ethoxy*-compound forms yellow needles melting at  $144-145^{\circ}$ .

*Paramethoxythiobenzo- $\beta$ -naphthalide* forms yellow plates melting at  $158-159^{\circ}$ ; the corresponding *ethoxy*-compound melts at  $148-149^{\circ}$ .

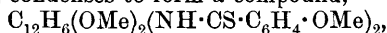
Metaphenylenedithiocarbimide, with anisole, gives a compound forming small, yellow needles melting at  $218-219^{\circ}$ ; the corresponding *ethoxy*-compound, prepared from phenetole, is similar, and melts at  $233^{\circ}$ .

Paraphenylenedithiocarbimide, with anisole and phenetole, give similar compounds crystallising in yellow needles melting respectively at  $281^{\circ}$  and  $293^{\circ}$ .

*Benzidinedithiocarbimide*, prepared in a similar manner to meta-bromophenylthiocarbimide, melts at  $203^{\circ}$ ; with anisole and phenetole, it gives compounds crystallising in yellow needles and melting at  $302-303^{\circ}$  and  $293^{\circ}$  respectively.

Orthotolidinedithiocarbimide, with anisole, gives the compound  $C_{12}H_6Me_2(NH \cdot CS \cdot C_6H_4 \cdot OMe)_2$ , which crystallises in yellow needles melting at  $250-252^{\circ}$ ; the corresponding *ethoxy*-compound melts at  $235-236^{\circ}$ .

*Dianisylidithiocarbimide*, prepared by the action of thiophosgene on dianisidine, crystallises in yellowish leaflets melting at  $192-194^{\circ}$ , and, with anisole, condenses to form a compound,



which crystallises in yellow needles melting at  $222-224^{\circ}$ ; the *ethoxy*-compound, prepared from phenetole, forms leaflets melting at  $233-235^{\circ}$ .

The yields in all cases are good, with the one exception of that from benzene and phenylthiocarbimide.

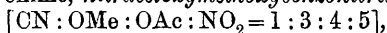
R. H. P.

**Action of Thiocarbanilide on Acid Anhydrides.** By FREDERICK L. DUNLAP (*Amer. Chem. J.*, 1899, 21, 528-530. Compare Abstr., 1897, i, 471).—By heating together molecular proportions of thiocarbanilide and succinic anhydride, the products previously obtained were succinanil, carbon oxysulphide, and aniline, but by keeping the temperature at  $95-96^{\circ}$ , the products are phenylthiocarbimide and succinanilic acid melting at  $144.5-145.5^{\circ}$ . The intermediate additive product, which could not be obtained in this case, was isolated when maleic anhydride was used in place of succinic anhydride. *Diphenylthiomaleuric acid*,  $COOH \cdot CH : CH \cdot CO \cdot NPh \cdot CS \cdot NPh$ , crystallises from alcohol in short, flat, transparent prisms and melts at  $160^{\circ}$ ; it is readily soluble in acetone, very sparingly so in ether or chloroform, and insoluble in benzene, light petroleum, carbon bisulphide, or water; it forms crystalline, barium, calcium, silver, potassium, and sodium salts. When the temperature is raised to  $180^{\circ}$ , the mixture begins to liberate carbon oxysulphide, and the gas is still more rapidly evolved when the temperature is raised to  $200^{\circ}$  or above.

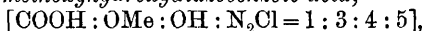
T. M. L.

**Nitrovanillin.** By WALTHER VOGL (*Monatsh.*, 1899, 20, 382-400).— *$\beta$ -Nitrovanillin* or *5-nitro-4-hydroxy-3-methoxybenzaldehyde*, prepared

by the action of nitric acid saturated with nitrous acid on an ethereal solution of vanillin at  $10^{\circ}$ , separates from boiling glacial acetic acid in pale yellow, crystalline nodules, melts at  $172^{\circ}$ , is almost insoluble in water, rather more soluble in boiling alcohol or ether, and easily soluble in hot glacial acetic acid. It dissolves in dilute aqueous solutions of the hydroxides or carbonates of the alkalis, forming yellow solutions. The potassium salt resembles potassium dichromate in appearance. The *acetyl* derivative separates in pale yellow crystals and melts at  $88^{\circ}$ . The *oxime* crystallises from boiling alcohol in lustrous, yellow needles, melts at  $200-201^{\circ}$ , and is almost insoluble in water, but easily soluble in ether and alcohol. By the action of acetic anhydride on the oxime, *nitracetoxymethoxybenzonitrile*,



is formed; it separates from alcohol as a white, crystalline mass with a tinge of yellow, melts at  $102^{\circ}$ , is easily soluble in ether, ethylic acetate, or glacial acetic acid, and less so in benzene. The corresponding acid, *nitrohydroxymethoxybenzoic acid*, or  *$\beta$ -nitrovanillic acid*, prepared by hydrolysing the nitrile, crystallises from glacial acetic acid in small, yellow leaflets often grouped in rosette-like clusters, melts at  $209-210^{\circ}$  without decomposing, and is sparingly soluble in hot water but easily so in alcohol. This compound is apparently not identical with Tiemann's nitrovanillic acid (this Journal, 1876, ii, 524). The corresponding  *$\beta$ -amidovanillic acid*, obtained by reducing the nitro-acid with tin and hydrochloric acid, separates as the hydrochloride in white, lustrous scales, becomes coloured at  $200^{\circ}$ , but does not melt below  $250^{\circ}$ , is easily soluble in alcohol and ether, and yields a platino-chloride,  $2\text{C}_8\text{H}_7\text{O}_4\cdot\text{NH}_2\cdot\text{H}_2\text{PtCl}_6$ . The *acetyl* derivative melts at  $215^{\circ}$ . The chloride of *methoxyhydroxydiazobenzoic acid*,

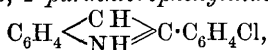


prepared by diazotising the amido-acid, crystallises from concentrated hydrochloric acid, decomposes with liberation of gas when gently heated, and is very sparingly soluble in water. When boiled with a very dilute solution of sodium carbonate in water, it forms *methoxygallic acid*,  $[\text{COOH}:\text{OMe}:(\text{OH})_2 = 1:3:4:5]$ , and vanillic acid. The former crystallises from xylene in yellowish-white needles, melts at  $199-200^{\circ}$ , is easily soluble in boiling water, and soluble in alcohol or ethylic acetate; with ferric chloride, the aqueous solution gives a bluish-black coloration, which, on the addition of sodium carbonate, becomes first violet and then bluish-red. The vanillic acid, which melts at  $206^{\circ}$ , probably results from the formation of a dicarboxylic acid by the replacement of the diazo-group by carboxyl and the subsequent loss of carbonic anhydride by this acid. Attempts to obtain an amido-product from nitrovanillin by reducing it with tin and hydrochloric acid or with stannous chloride resulted for the most part in the formation of unstable or tarry products.

E. W. W.

**Action of Parachloro- and Parabromo-phenyl Bromomethyl Ketones on Aniline.** By A. COLLET (*Bull. Soc. Chim.*, 1899, [iii], 21, 65-67. Compare Abstr., 1898, i, 123, 139, 447).—*Parachlorophenyl anilidomethyl ketone*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHPh}$ , obtained by heating together aniline and parachlorophenyl bromomethyl ketone in alcoholic solution, crystallises from alcohol and chloroform

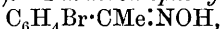
in bright yellow needles melting at 187—188°; when the ketone is added to boiling aniline, 1'-*parachlorophenylindole*,



is produced; this crystallises from alcohol in colourless leaflets and melts at 201—202° (compare Bischler, *Abstr.*, 1892, 1465; Kuncell, *Abstr.*, 1897, i, 282).

*Parabromophenyl anilidomethyl ketone* melts at 119—120°; 1'-*parabromophenylindole* melts at 208—209°; these compounds resemble the corresponding chloro-derivatives. G. T. M.

**Parabromophenyl Methyl Ketone.** By A. COLLET (*Bull. Soc. Chim.*, 1899, [iii], 67—68).—*Parabromophenyl methyl ketoxime*,



crystallises from alcohol in long, colourless needles and melts at 128°; when heated at 100° with concentrated sulphuric acid, it is converted into parabromacetanilide. When parabromophenyl methyl ketone is treated with bromine (1 mol.), parabromophenyl bromomethyl ketone is produced, and this substance, when oxidised with alkaline potassium permanganate, yields parabromophenylglyoxylic acid,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{COOH}$  (Rupe, *Abstr.*, 1892, i, 218).

*Parabromophenyl dibromomethyl ketone*,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CO} \cdot \text{CHBr}_2$ , is obtained when 2 mols. of bromine are employed; it separates from alcohol in colourless crystals melting at 92—93°, is oxidised by permanganate to parabromobenzoic acid, and when treated with excess of potash, parabromophenylglycollic acid,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ , is produced. G. T. M.

**Parachlorophenyl Methyl Ketone.** By A. COLLET (*Bull. Soc. Chim.*, 1899, [iii], 21, 68—70).—Parachlorophenyl methyl ketone is most readily prepared by mixing together acetic chloride, chlorobenzene, and aluminium chloride, a yield of 55 per cent. being obtained. The *oxime*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CMe} \cdot \text{NOH}$ , crystallises in colourless needles melting at 95°, and on treatment with warm concentrated sulphuric acid is converted into parachloracetanilide. The *phenylhydrazone* crystallises in yellow needles and melts at 114°. Parachlorophenyl bromomethyl ketone is prepared by adding bromine (1 mol.) to parachlorophenyl methyl ketone dissolved in carbon bisulphide, and is identical with that obtained from bromoacetic chloride and chlorobenzene.

*Parachlorophenylglyoxylic acid*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CO} \cdot \text{COOH}$ , obtained by oxidising parachlorophenyl bromomethyl ketone with permanganate, separates from alcohol in colourless crystals.

*Parachlorophenyl dibromomethyl ketone*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CO} \cdot \text{CHBr}_2$ , produced by adding bromine (2 mols.) to parachlorophenyl methyl ketone dissolved in carbon bisulphide, separates from alcohol in colourless crystals melting at 92·5°.

*Parachlorophenylglycollic acid*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ , obtained by mixing the preceding compound with 10 per cent. caustic potash, crystallises from benzene in colourless needles melting at 112—113°.

G. T. M.

**Bromophenacetin.** By WILHELM VAUBEL (*Ber.*, 1899, 32, 1875).—A claim for priority. T. M. L.

**Orthohydroxyphenoxyacetic Acid and Orthophenylene-dioxyacetic Acid.** By CHARLES MOUREU (*Bull. Soc. Chim.*, 1899, [iii], 21, 107—109).—The intense blue coloration produced on adding ferric chloride to a solution of orthohydroxyphenoxyacetic acid (see this vol., i, 679) disappears on neutralisation, and this fact is made use of in the alkalimetric estimation of the acid.

In the preparation of orthohydroxyphenoxyacetic acid by the condensation of chloroacetic acid with catechol, *orthophenylenedioxydiacetic acid*,  $C_6H_4(O\cdot CH_2\cdot COOH)_2$ , is also formed; this crystallises from boiling water in slender needles melting at 172—174°. N. L.

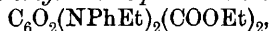
**Action of Sulphuryl Chloride on Alkyl Hydroxybenzoates.** By GIROLAMO MAZZARA (*Gazzetta*, 1899, 29, i, 340—347).—Ethylic 5-chlorosalicylate,  $OH\cdot C_6H_3Cl\cdot COOEt$ , obtained by the action of sulphuryl chloride on ethylic salicylate, crystallises in long, lustrous needles melting at 25°. Smith and Macchall (*Abstr.*, 1878, 879) gave the melting point as 110°, although in both cases the products give rise to the same chlorosalicylamide melting at 223°. As methylic 5-chlorosalicylate melts at 48·5°, the lower temperature is probably correct for the ethylic salt, since the ethylic derivatives of such acids are, in general, more volatile than the corresponding methylic salts.

*Ethylic 5-chloro-2-ethoxybenzoate*,  $OEt\cdot C_6H_3Cl\cdot COOEt$ , prepared by heating under pressure a mixture of ethylic 5-chlorosalicylate, potassium hydroxide, and ethylic iodide in presence of absolute alcohol, boils at 226° under 55 mm. pressure, and when cooled by means of salt and snow, solidifies to a crystalline mass which liquefies at ordinary temperatures. Free *5-chloro-2-ethoxybenzoic acid*, obtained by hydrolysing the ethylic salt with 40 per cent. potash, crystallises from dilute alcohol in shining, white laminæ melting at 118°.

No trace of dichlorosalicylic acid is obtained by the action of an excess of sulphuryl chloride on ethylic salicylate. T. H. P.

**Derivatives of Ethylic Succinylsuccinate.** By J. GUINCHARD (*Ber.*, 1899, 32, 1742—1744. Compare Hantzsch and Zeckendorf, *Abstr.*, 1888, 278; Hantzsch and Hermann, *ibid.*, 954; Böniger, *ibid.*, 954).—*Ethylic di-iodoquinoldicarboxylate*,  $C_6I_2(OH)_2(COOEt)_2$ , separates from benzene in colourless needles and melts at 167°. The crystals of the substance are always white, but solutions in benzene, ether, or chloroform are deep green, and only the alcoholic solution is colourless when cooled with a freezing mixture; the fused substance is also green before it begins to decompose, owing to the formation of the isodynamic quinonoid modification. *Ethylic di-iodoquinonedicarboxylate*,  $C_6I_2O_2(COOEt)_2$  the product of oxidation with nitric acid in alcoholic solution, crystallises in small, orange-coloured needles, melts and decomposes at 231°, dissolves slightly in alcohol or ether, and readily in benzene. *Ethylic dipiperidoquinonedicarboxylate*,  $C_6O_2(C_5H_{10}N)_2(COOEt)_2$ , forms fine dark violet crystals, melts at 148°, dissolves readily in alcohol or benzene and slightly in water, does not form salts with acids, is

hydrolysed by sodium hydroxide to piperidine and ethylic dihydroxy-quinonedicarboxylate, and when reduced yields ethylic tetrahydroxy-terephthalate. *Ethylic ethylanilidoquinonedicarboxylate*,



crystallises from alcohol in reddish-violet needles and melts at  $182^\circ$ .

Ethylic dibromoquinoldicarboxylate forms an *additive* compound with two mols. of zinc ethyl. T. M. L.

**Action of Benzenesulphonic Chloride on Asymmetrical Alkylphenylhydrazines.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1804—1805).—Hinsberg's method for the separation of primary and secondary amines by the aid of benzenesulphonic chloride cannot always be employed with success. For example, methylphenylhydrazine in addition to giving the normal monosulphonyl derivative,



melting at  $131\cdot5$ — $132^\circ$  and soluble in alkali (*Ber.*, 1894, 27, 372), also yields a *dibenzenesulphonylmethylphenylhydrazine*,  $\text{NMePh}\cdot\text{N}(\text{SO}_2\text{Ph})_2$ , which crystallises in hard, glistening prisms melting at  $169$ — $170^\circ$ , and is insoluble in alkali; the same compound is readily obtained when the monosulphonyl derivative is treated according to the Schotten-Baumann method with benzenesulphonic chloride. Ethylphenylhydrazine reacts in a similar manner, yielding a mixture of the *monobenzenesulphonyl* derivative soluble in alkali and melting at  $96^\circ$ , and of the *dibenzenesulphonyl* compound melting at  $140$ — $141^\circ$  and insoluble in alkali. Benzenesulphonemethylphenylhydrazine, when shaken with benzoic chloride and alkali, yields the benzoyl derivative  $\text{NMePh}\cdot\text{NBz}\cdot\text{SO}_2\text{Ph}$ , melting at  $119^\circ$ . (Compare Solonina, *J. Russ. Chem. Soc.*, 1897, 29, 404.) J. J. S.

**The So-called Benzil Reaction.** By EUGEN BAMBERGER and ROLAND SCHOLL (*Ber.*, 1899, 32, 1809—1810).—The colour reaction for 1 : 2-diketones previously described (Bamberger, *Abstr.*, 1885, 807) is not given by pure benzil, but is instantaneously produced when a minute quantity of benzoin is present. This reaction (the benzil-benzoin reaction) can therefore be made use of in testing for either benzil or benzoin. J. J. S.

**Hydroxydiphenylene Ketone and Orthophenylsalicylic Acid.** By GEORG HEYL (*J. pr. Chem.*, 1899, [ii], 59, 434—463. Compare this vol., i, 216; also Staedel, *Abstr.*, 1895, i, 233).—Symmetrical diorthamidobenzophenone is best prepared by the reduction with iron powder of symmetrical diorthonitrobenzophenone dissolved in glacial acetic acid, a small quantity of *symmetrical ortho-nitroorthamidobenzophenone* being obtained as a bye-product; this crystallises in yellow needles melting at  $149$ — $150^\circ$ . The *sodium*, *potassium*, *ammonium*, and *silver* salts of hydroxydiphenylene ketone are described; the *sodium* salt crystallises from water in characteristic lustrous, reddish-yellow plates.

Orthophenylsalicylic acid, which crystallises from water and melts at  $195^\circ$ , can be distinguished from salicylic acid by its yielding a deep red liquid on treatment with cold concentrated sulphuric acid, from

which solution a yellow precipitate of hydroxydiphenylene ketone can be obtained on the addition of water. Under similar treatment, salicylic acid is recovered unchanged; further, the red coloration formed on adding hydrogen peroxide to a solution of sodium salicylate is not given by sodium orthophenylsalicylate.

The *silver* and *potassium* salts of orthophenylsalicylic acid are described. R. H. P.

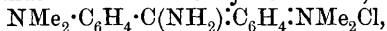
**Imines of Benzophenone and the Constitution of Auramine.** By CARL GRAEBE (*Ber.*, 1899, 32, 1678—1783).—The substance prepared by the action of ammonia on 2 : 2'-dihydroxybenzophenone and formulated as  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$  (Abstr., 1892, 1227), is shown to be 2 : 2'-dihydroxybenzophenonimine,  $\text{NH} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2$ , since it is hydrolysed by dilute hydrochloric acid to 2 : 2'-dihydroxybenzophenone and ammonia, and does not yield a diazo-compound.

As is shown in the following abstract and this vol., i, 705, aniline condenses directly at 195—200° with most derivatives of benzophenone which are substituted in one of the ortho-positions, giving rise to the corresponding benzophenonephenylimine derivative; 2 : 2'-dihydroxybenzophenone, however, loses a second molecule of water and gives

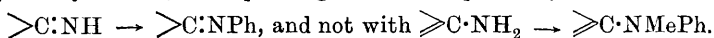
xanthonephenylimine,  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} : \text{NPh}$ . Condensation does not occur under these conditions with benzophenone, meta- and para-hydroxybenzophenone, meta- and para-chlorobenzophenone, orthonitrobenzophenone, orthamidobenzophenone and 4 : 4'-dihydroxybenzophenone.

Benzophenonephenylimine,  $\text{NPh} : \text{CPh}_2$ , is usually prepared from benzophenone chloride, but direct condensation occurs when benzophenone is heated at 240—250° in a flask with a long neck and three or four times its weight of aniline is gradually added from a dropping funnel. Under similar conditions, 4 : 4'-dihydroxybenzophenone also gives an orange-yellow phenylimine.

Benzophenone and all its derivatives are yellow and give yellow salts; with hydrogen sulphide, the phenylimine group is replaced by sulphur. Their behaviour is quite similar to that of auramine, and the latter is therefore regarded as a ketone-imine,  $\text{NH} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ . The salts of auramine are also regarded as ketone-imines, and not as quinonoid in structure (Stock, Abstr., 1893, i, 472), since the difference in colour between the base and its salts is only small, corresponding with that which exists between hydroxybenzophenone and its salts, and much less than that between acridine and its salts. Moreover, the quinonoid formula for auramine hydrochloride,



differs only from that of malachite-green in the replacement of  $-\text{C}_6\text{H}_5$  by  $-\text{NH}_2$ , and the salts might therefore be expected to have a green to blue colour. Finally auramine hydrochloride is readily converted into phenylauramine by heating with aniline, but is not attacked by methylaniline, corresponding with the expression,



T. M. L.



**Ortho-derivatives of Benzophenonephenylimine.** By CARL GRAEBE and F. KELLER (*Ber.*, 1899, 32, 1683—1688).—*Orthohydroxybenzophenonephenylimine*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh:NPh}$ , crystallises in stout needles of an intense golden-yellow colour, melts at  $138\cdot5^\circ$  (corr.), does not dissolve in water but dissolves readily in hot alcohol; it does not dissolve in aqueous alkalis, but remains in solution when a drop of soda is added to the alcoholic solution and an excess of water is then added; it dissolves in an 18 per cent. solution of hydrogen chloride, but is thrown down again unchanged on adding an excess of water. On heating with hydrochloric acid, or with water at  $150^\circ$ , it is decomposed into aniline and orthohydroxybenzophenone. The *acetyl* derivative crystallises from alcohol in colourless flakes and melts at  $129^\circ$ ; its *hydrochloride* is a yellow salt; on boiling with water, it is decomposed into hydroxybenzophenone, acetic acid, and aniline. *Orthomethoxybenzophenonephenylimine* crystallises from alcohol in yellow needles and melts at  $77^\circ$ ; its alcoholic solution is precipitated on adding soda and excess of water, but towards hydrochloric acid it behaves like the hydroxy-compound.

2 : 4'-*Dihydroxybenzophenonephenylimine* crystallises from alcohol in dark yellow needles and melts at  $214^\circ$ ; it dissolves slowly in alkalis at ordinary temperatures, but loses aniline when heated; it forms a yellow *hydrochloride* which is decomposed on boiling with water; the molecular weight, determined from the freezing point of a solution in phenol, is normal. The *diacetyl* derivative is greenish-yellow, and forms a bright yellow *hydrochloride*.

2 : 3 : 4'-*Trihydroxybenzophenonephenylimine* melts at  $95^\circ$ , is not soluble in water, but dissolves readily in alcohol and in alkalis to a yellow solution; 18 per cent. hydrochloric acid dissolves it, but the yellow solution is decomposed on boiling.

Orthochlorobenzophenone readily solidifies when pure and melts at  $45\cdot5^\circ$ , it boils at  $330^\circ$  (corr.) and crystallises from a mixture of chloroform and light petroleum in well-formed tablets. *Orthochlorobenzophenonephenylimine* crystallises from alcohol in yellow needles, melts at  $128^\circ$  and dissolves readily in chloroform; it dissolves in moderately concentrated hydrochloric acid to a yellow solution, but on heating, the colour disappears and orthochlorobenzophenone separates; on heating with an alcoholic solution of hydrogen sulphide, it gives a mixture of chlorobenzophenone and chlorothiobenzophenone.

*Orthomethylbenzophenonephenylimine* melts at  $104\cdot5^\circ$ , and crystallises from alcohol in stout, yellow needles. T. M. L.

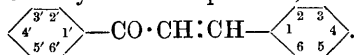
**Decomposition of Homologues of Benzophenone by Halogen Acids.** By MAX WEILER (*Ber.*, 1899, 32, 1908—1911).—When mesitylmesitylene,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$  [2 : 4 : 6 : 3' : 5'], is heated for 8 hours with concentrated hydriodic acid and phosphorus at  $160$ — $180^\circ$ , it is decomposed to the extent of 50 per cent. into mesitylene and mesitylenic acid, a small proportion only of *pentamethyldiphenylmethane* being obtained in the form of flat needles melting at  $67$ — $68^\circ$ . This fact is of interest since benzophenone (Graebe, *Abstr.*, 1875, 457), meta- and paramethylbenzophenone, diparatolylketone (Ador and Rilliet, *Ber.*, 1879, 2298), parethylbenzophenone, and 4-benzoylmetaxylene (Söllscher, *Abstr.*, 1882, 1292) yield only the

corresponding diphenylmethanes on treatment with hydriodic acid. Concentrated hydrochloric acid at 150—160° hydrolyses mesitoyl-mesitylene to the extent of 15 per cent., and benzoylmesitylene to the extent of 40 per cent., at 190°; moreover, the latter yields 62 per cent. of the benzoic acid and mesitylene required by theory when heated with concentrated hydrobromic acid of sp. gr. 1·49 for 18 hours at 190°. No hydrolysis, however, occurs when the compounds mentioned are boiled with alcoholic soda or with sodium dissolved in amyl alcohol; they are easily reduced, however, to the corresponding hydrols by zinc dust and dilute alcoholic potash, and these are then easily converted into the corresponding diphenylmethanes by reduction with hydriodic acid in presence of phosphorus.

The author summarises his results and those of a similar nature obtained by others (Louise, *Ann. Chim. Phys.*, 1885, [vi], 6, 206; Elbs, *Abstr.*, 1887, 940; Victor Meyer, *Abstr.*, 1895, i, 466, and Muhr, *ibid.*, i, 231) in the generalisation that orthomethylbenzophenones are easily hydrolysed by acids to the corresponding orthomethylated hydrocarbon and the carboxylic acid of the other radicle; thus the action  $\text{ArMe}\cdot\text{CO}\cdot\text{Ar} + \text{H}_2\text{O} = \text{ArHMe} + \text{Ar}\cdot\text{COOH}$  takes place, although that expressed by the equation  $\text{ArMe}\cdot\text{CO}\cdot\text{Ar} + \text{H}_2\text{O} = \text{ArMe}\cdot\text{COOH} + \text{ArH}$ , never occurs.

Mesitoyl chloride (Fittig and Brückner, *Annalen*, 1868, 147, 47), when pure, is a strongly refracting oil, which boils at 109·5° under 10 mm. pressure; *mesitoylmesitylene* (*dimesityl ketone*),  $\text{C}_{18}\text{H}_{20}\text{O}$ , prepared by the action of aluminiumchloride on a solution of mesitylene and mesitoyl chloride in carbon bisulphide, crystallises from alcohol in colourless, stellar aggregates of prisms, and melts at 84—85°. W. A. D.

**The Six Isomeric Monohydroxybenzylideneacetophenones. (Monohydroxychalkones).** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1899, 32, 1921—1926).—It is proposed to apply the name *chalkone* to benzylideneacetophenone,



The properties of the six hydroxychalkones are shown in the following table:

	Crystals.	M. p.	Solution in alkali.	Solution in $\text{H}_2\text{SO}_4$ .	M. p. of acetyl derivative
2'-Hydroxychalkone	{ Yellow needles. }	88—89°	Orange	Yellow	51—52°
3'-Hydroxychalkone.	{ Pale-yellow tablets. }	126	Yellow	{ Yellowish-red }	101
4'-Hydroxychalkone.	{ Yellow needles. }	172—173	„	„	90
2-Hydroxychalkone	{ Yellow flakes. }	153—155	{ Yellowish-red }	„	68—69
3-Hydroxychalkone	{ White flakes. }	159—160	{ Pale yellow }	Yellow	102—103
4-Hydroxychalkone	{ Pale-yellow scales. }	182—183	{ Deep yellow }	Orange	129—131

It will be seen that the orthohydroxy-compounds are more intensely coloured than the para-compounds, and that the meta-compounds are less strongly coloured. The influence of the hydroxyl group is more pronounced in the aldehyde residue than in the ketone residue. The metahydroxy-compounds have been shown to have the lightest colour in the case of the three monohydroxybenzylideneindanediones,

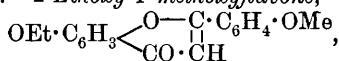
$C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:CH \cdot C_6H_4 \cdot OH$ , and the three monohydroxybenzylidene-

bromindanones,  $C_6H_3Br \begin{smallmatrix} \diagup CH_2 \\ \diagdown CO \end{smallmatrix} C:CH \cdot C_6H_4 \cdot OH$ , but in the case

of the hydroxyxanthenes and the three nitrophenols the metahydroxy-compounds have an intermediate tint (Abstr., 1898, 32, 271; 1893, i, 217). T. M. L.

**2:4'-Dihydroxyflavone.** By STANISLAUS VON KOSTANECKI and S. ODERFELD (*Ber.*, 1899, 32, 1926—1930. Compare this vol., i, 370).—**2':5'-Diethoxy-4-methoxychalkone**,  $C_6H_3(OEt)_2 \cdot CO \cdot CH:CH \cdot C_6H_4 \cdot OMe$ , prepared from 2:5-diethoxyacetophenone and anisaldehyde, crystallises from alcohol in yellow needles, melts at 76.5—77.5°, and is coloured dark-red by concentrated sulphuric acid, giving a yellowish-red solution. **2-Ethoxy-4'-methoxyflavanone**,  $OEt \cdot C_6H_3 \begin{smallmatrix} \diagup O-CH \cdot C_6H_4 \cdot OMe \\ \diagdown CO \cdot CH_2 \end{smallmatrix}$ ,

from 2-hydroxy-5-ethoxyacetophenone and anisaldehyde, crystallises from alcohol in long, colourless needles and melts at 131—132°; it dissolves in alcohol with a blue fluorescence, in concentrated sulphuric acid with a yellowish-red colour, and in alcoholic potash to a red solution from which water precipitates the original compound. The *monobromo*-compound crystallises from alcohol in white needles and melts at 140—141°. **2-Ethoxy-4'-methoxyflavone**,



crystallises from dilute alcohol in very pale, yellowish, monohydrated needles; the yellow tint is probably due to impurities, since diethoxyflavone is colourless; the anhydrous substance melts at 134—135°, and dissolves in concentrated sulphuric acid to a pale yellow solution with a green fluorescence; sodium ethoxide decomposes it into 2-hydroxy-4-ethoxyacetophenone and anisic acid. By heating with concentrated hydriodic acid, it is converted into **2:4'-dihydroxyflavone**, which crystallises from alcohol in slender, colourless needles, and chars at 320° without melting; concentrated sulphuric acid colours the crystals yellow, and gives a pale yellow solution with a slight green fluorescence; it dissolves in caustic soda to a greenish-yellow solution. The *diacetate* crystallises from a mixture of alcohol and acetic acid in white needles, and melts at 207°. **2:4'-Diethoxyflavone** crystallises from alcohol in pure white needles and melts at 143°; concentrated sulphuric acid colours the crystals yellow, and gives a pale yellow solution with a fine green fluorescence.

T. M. L.

**Oxime and Phenylhydrazone of Xanthone.** By CARL GRAEBE and PAUL RÖDER (*Ber.*, 1899, 32, 1688—1690).—*Xanthonephenylimine*,

$\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C:NPh}$ , separates from alcohol in golden-yellow crystals and melts at  $134.5^\circ$ ; it dissolves in concentrated sulphuric acid with a yellow colour and a green fluorescence, dissolves in concentrated hydrochloric acid, and gives a deep yellow *hydrochloride* which is decomposed by boiling water into xanthone and aniline, does not dissolve in alkalis, and is reduced to xanthen by heating with zinc dust. By boiling with an alcoholic solution of hydrogen sulphide it is converted into *xanthione*,  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{CS}$ , isomeric with Graebe and Schulthess' thioxanthone,  $\text{S} \langle \text{C}_6\text{H}_4 \rangle \text{CO}$ ; this melts at  $156^\circ$  and crystallises in long, dichroic needles which appear either dark red or brownish-red; it is yellow by transmitted light, and is also precipitated as a yellow powder on adding water to an alcoholic solution; the alcoholic solution is green, but, by reason of a strong fluorescence, appears red, or reddish-brown; it is very readily soluble in carbon bisulphide, and gives an intensely green solution with but slight fluorescence; concentrated sulphuric acid dissolves it to a yellow solution with a green fluorescence. *Xanthoneoxime*,  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C:NOH}$ , prepared by the action of hydroxylamine on xanthione, forms colourless crystals, melts at  $161^\circ$ , and dissolves in concentrated sulphuric acid to a yellow solution with a blue fluorescence; it dissolves in hydrochloric acid, but is reprecipitated by water, and on boiling the solution xanthone is formed; it dissolves only with difficulty in caustic alkalis. *Xanthonephenylhydrazone*,  $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C:N.NHPh}$ , prepared by the action of phenylhydrazine on xanthione, crystallises from alcohol in golden-yellow needles and melts at  $152^\circ$ ; it dissolves in concentrated sulphuric acid to a yellow solution with a green fluorescence; concentrated hydrochloric acid converts it into an orange-yellow *hydrochloride*, which dissolves on warming to an orange-yellow solution; on boiling the solution, it is decomposed and xanthone separates in colourless or yellowish needles. T. M. L.

**Hydroxylamine Derivatives of Tetrahydropyrone Compounds.** By PAWEŁ IW. PETRENKO-KRITSCHENKO and S. ROSENZWEIG (*Ber.*, 1899, 32, 1744—1748).—The *oxime* of orthodiethoxydiphenyltetrahydropyrone,  $\text{O} \langle \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OEt}) \cdot \text{CH}_2 \rangle \text{C:NOH}$  (this vol., i, 440), melts at  $133^\circ$ ; it crystallises with 1 mol. of ethylic alcohol, acetic acid, pyridine, methylic alcohol, acetone, or chloroform; the first three compounds have an indeterminate melting point at  $109^\circ$ ,  $109^\circ$ , and  $85^\circ$  respectively; in all cases the molecule of solvent is expelled readily by drying (at  $100^\circ$ ?). When a solution of the oxime in chloroform, acetic acid, or acetone is saturated with hydrogen chloride and allowed to crystallise, the *hydrochloride* of the oxime is obtained; this melts and decomposes at  $154^\circ$ .

The *oximes* of orthodimethoxydiphenyltetrahydropyrone (*loc. cit.*)

and diphenyltetrahydropyrone (this vol., 1897, i, 142), which melt at  $202^{\circ}$  and  $154^{\circ}$ , yield additive products in the same way.

These oximes are obtained quite readily; on the other hand, tetrahydropyrones in which an H of each  $\text{CH}_2$  group has been replaced, for example, by  $\text{COOEt}$ , do not yield oximes. C. F. B.

**Constitution of Phenolphthalein.** By HANS MEYER (*Monatsh.*, 1899, 20, 337—368).—When phenolphthalein oxime, suspended in alcohol, is heated with a concentrated aqueous solution of hydroxylamine hydrochloride, parahydroxyphthalanil,  $\text{C}_6\text{H}_4[\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2$ , identical with Piutti's compound (Abstr., 1886, 1026), is formed; it crystallises in small, colourless scales with a silvery lustre, melts at  $292^{\circ}$  (Piutti gave  $287^{\circ}$ ), is easily soluble in boiling alcohol, soluble in ether or ethylic acetate, and insoluble in water. Its solutions in fixed alkalis are yellow; its solution in ammonia is colourless, but becomes violet when exposed to the air, probably owing to partial conversion into phthalimide and amidophenol, for the latter compound gives the same reaction. The acetyl derivative of parahydroxyphthalanil melts at  $237^{\circ}$ . By the action of dilute hydrochloric or sulphuric acid, parahydroxyphthalanil is decomposed into phthalic acid and amidophenol. Since hydroxybenzoylbenzoic acid does not react with hydroxylamine hydrochloride in alkaline or neutral solution, the formation of hydroxyphthalanil must be due to the intermediate production of the dioxime of phenolphthalein.

*Parahydroxyphenylphthalazone*,  $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{C}(\text{C}_6\text{H}_4\cdot\text{OH}) \\ \text{CO} \end{array}\right\rangle\text{NPh}$ , is formed, together with amidophenol, by gently warming phenolphthalein-monoxime with phenylhydrazine, acetic acid, and alcohol or water for a short time, and is also obtained by the action of phenylhydrazine on hydroxybenzoylbenzoic acid; it forms small, colourless needles which gradually become yellow or green when exposed to the light, melts at  $272^{\circ}$ , is easily soluble in boiling alcohol, sparingly so in alkalis, insoluble in water or acids, and forms a yellow solution in concentrated sulphuric acid.

By the action of aqueous or alcoholic ammonia on phenolphthalein at the ordinary temperature, iminophenolphthalein (Errera and Gasparini, Abstr., 1894, i, 294) is formed, together with a small quantity of gummy or amorphous substances which contain nitrogen.

When an alcoholic solution of orthohydroxybenzoylbenzoic acid is reduced with zinc and hydrochloric acid, Bistrzycki and Oehlert's hydroxyphenylphthalide (Abstr., 1897, i, 600) is obtained; it melts at  $157$ — $160^{\circ}$ , not at  $148$ — $151^{\circ}$ , and by melting a mixture of this substance with paramidophenol, a compound melting at  $252$ — $256^{\circ}$ , and identical with that prepared by reducing phenolphthalein itself, is formed. Hence phenolphthalein in coloured alkaline solutions has a symmetrical constitution,  $\text{C}_6\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OK})_2$ , whilst in neutral or colourless alkaline solutions it reacts as a lactone,  $\text{CO}\left\langle\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{O} \end{array}\right\rangle\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$ .

The change from the lactone to the diketone form corresponds with that of unsaturated phthalides into diketohydrindene derivatives, and the reverse change resembles the intramolecular rearrangement of

benzilic acid. The phthaleins which are insoluble in alkalis are also converted into the coloured, symmetrically constituted, forms by the action of concentrated acids.

Diphthalyllic acid forms two diethylic salts, a coloured and a colourless one, and there are two modifications of benzilcarboxylic acid, of which one is colourless and the other yellow. E. W. W.

**Acetylation of  $\alpha$ -Naphthylamine.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1803—1804. Compare Gattermann, this vol., i, 516).—In the preparation of acetyl- $\alpha$ -naphthylamine by Gattermann's method, a considerable quantity (in some cases over 50 per cent. of the base employed) of the *diacetyl* derivative,  $C_{10}H_7NAc_2$ , is always formed; it is characterised by the readiness with which it crystallises, yielding clear, rhombic prisms melting at 128—129°, and soluble in light petroleum or alcohol.  $\beta$ -Naphthylamine and aniline also yield diacetyl derivatives when heated with acetic anhydride, but only in small quantities. J. J. S.

**Isomeric Naphthalene Derivatives.** By PAUL FRIEDLÄNDER, H. HEILPERN, and M. SPIELFOGEL (*Chem. Centr.*, 1899, i, 288—289; from *Mitt. Technol. Gewerb.-Mus., Wien*, [ii], 8, 316—323).—1:2-Nitronaphthylamine is best prepared by adding concentrated nitric acid to  $\beta$ -acetonnaphthalide suspended in ice-cold glacial acetic acid; the 1:2-nitracetonnaphthalide formed is extracted with benzene and then hydrolysed by boiling with alcoholic potash. 1:2-Nitronaphthylamine may also be obtained by the action of concentrated nitric acid on  $\beta$ -naphthyloxamic acid below 40°.  $\beta$ -Naphthyloxamic acid, prepared by heating  $\beta$ -naphthylamine with oxalic acid at 140—150°, crystallises from glacial acetic acid in white leaflets, melts at 190°, is slightly soluble in water, readily in alcohol or ether, and forms easily soluble sodium and ammonium salts and sparingly soluble calcium and barium salts. 1:2-Nitronaphthonitrile, prepared by diazotising 1:2-nitronaphthylamine in alkaline solution and then treating with potassium cuprous cyanide, crystallises in light brown needles, melts at 101°, and is easily soluble in alcohol, benzene, or glacial acetic acid. 4:2-Nitronaphthoic acid, obtained by boiling 1:2-nitronaphthonitrile with baryta water for a long time, crystallises from chloroform in reddish needles, melts at 182°, and forms alkali salts which are easily soluble in water.

4':2-Nitronaphthonitrile is prepared from 4':2-nitronaphthylamine; it crystallises from 25 per cent. acetic acid solution in yellowish-brown, and from alcohol in copper-red, needles, melts at 168°, and by the action of dilute sulphuric acid at 150° forms 4':2-nitronaphthamide, which crystallises from acetone in brownish-yellow needles and melts at 261—263°. The corresponding 4':2-nitronaphthoic acid crystallises from alcohol in yellowish-white needles, melts at 286—287°, and is slightly soluble in alcohol, very slightly so in water, and easily in acetone; the ammonium, sodium, and barium salts crystallise in needles, the two former being easily, but the last only very slightly, soluble in water. This acid appears to be identical with that obtained by nitrating  $\beta$ -cyanonaphthalene. 1':2-Nitronaphthonitrile, prepared from the corresponding amine, crystallises from benzene and alcohol in needles, and melts at 143°. 1':2-Nitronaphthamide crystallises from

alcohol in brownish-yellow needles and melts at  $218^{\circ}$ . 1:2-*Nitronaphthoic acid* crystallises from alcohol in pale brown needles and melts at  $295^{\circ}$ .

1:4'-*Amidonaphthonitrile*, obtained by distilling a mixture of sodium naphthylaminesulphonate with potassium ferrocyanide, crystallises from acetic acid in greenish-yellow needles, melts at  $137^{\circ}$ , is slightly soluble in hot water, alcohol, or ether, and when hydrolysed with sulphuric acid (2:1) yields 1:4'-amidonaphthoic acid. 1:4'-*Hydroxynaphthoic acid*, prepared by treating a solution of 1:4'-amidonaphthoic acid with a diazotised solution of paranitraniline and boiling with a small quantity of carbamide, crystallises in small, white needles, melts at  $219^{\circ}$ , is easily soluble in acetic acid, alcohol, or ether, slightly so in water, and forms an insoluble copper salt. *Ethylic* 1:4'-*hydroxynaphthoate* crystallises from a mixture of benzene and light petroleum in small, white needles, melts at  $73^{\circ}$ , is easily soluble in alcohol, ether, or benzene, slightly so in light petroleum, and insoluble in water. 2:2'-*Amidonaphthonitrile* crystallises from toluene in pale yellow needles and melts at  $170-171^{\circ}$ . 2:2'-*Amidonaphthoic acid* crystallises in white needles and melts at  $245^{\circ}$ . 2:2'-*Hydroxynaphthoic acid* crystallises in leaflets and melts at  $245^{\circ}$ . 1:2'-*Amidonaphthonitrile* melts at  $117^{\circ}$ .  
E. W. W.

**Isomeric Naphthalene Derivatives.** By PAUL FRIEDLÄNDER and ARMIN FISCHER (*Chem. Centr.*, 1899, i, 289; from *Mitt. Technol. Gewerb.-Mus., Wien*, [ii], 8, 324—325).—Sodium hydrogen  $\beta$ -nitronaphthalenedisulphonate is prepared by adding 10 parts of a mixture of equal parts of nitric and sulphuric acids to 28 parts of powdered 1:4'-naphthalenedisulphonic acid suspended in 90 parts of sulphuric acid, the mixture being well cooled. The product, after remaining a short time, is poured on to ice and treated with 40 parts of sodium carbonate. Sodium  $\beta$ -naphthylaminedisulphonate, prepared by reducing the corresponding nitro-salt (German Patent, 65997), crystallises in broad, white needles, is easily soluble in hot water, very slightly in absolute alcohol, and may be salted out of its aqueous solution by means of sodium chloride; the alkaline solution has a bluish-violet fluorescence. The acid barium salt,  $[\text{HSO}_3 \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{SO}_3]_2\text{Ba}$ , prepared by boiling the solution of the sodium salt with a concentrated solution of barium chloride for a long time, crystallises in very small needles, and is slightly soluble in water.  $\beta$ -Naphthylaminedisulphonic acid,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$  [ $\text{SO}_3\text{H} : \text{NH}_2 : \text{SO}_3\text{H} = 1' : 2 : 4$ ], obtained by decomposing the barium salt with dilute sulphuric acid, crystallises in concentrically grouped prisms, and is slightly soluble in moderately concentrated sulphuric acid.  
E. W. W.

**Terpenes and Ethereal Oils.** Pinole. By OTTO WALLACH [WILHELM STIEHL, ADOLF SIEVERTS and R. SIEVERTS], *Annalen*, 1899, 306, 267—282. Compare Abstr., 1896, i, 571).—Although the constitution of pinole is well represented by the formula already given (Abstr., 1896, i, 101), certain anomalies present themselves in the behaviour of pinole tribromide, obtained by adding the elements of hydrogen bromide to pinole dibromide.

*Isopinole dibromide*,  $\text{C}_{10}\text{H}_{16}\text{Br}_2\text{O}$ , produced on eliminating hydrogen

bromide from pinole tribromide by means of quinoline in benzene, or of silver acetate in ethylic acetate, separates from ether in transparent, well-formed crystals, which differ in habit from the isomeride, but melt at  $94^{\circ}$ ; it is noteworthy that the substance is unsaturated, yielding pinole tribromide with hydrogen bromide, and with bromine the *tetrabromide*,  $C_{10}H_{16}Br_4O$ , which melts at  $132^{\circ}$ . When a solution of pinole tribromide in glacial acetic acid is digested with silver acetate, the compound  $C_{12}H_{20}Br_2O_3$  is produced; it crystallises from methylic alcohol and melts at  $118-120^{\circ}$ .

Hot 10 per cent. potassium hydroxide converts pinole tribromide and isopinole dibromide into inactive carvone, but sodium methoxide gives rise to the methylic ether of carveol or carvacrol.

*Pinolone*,  $C_{10}H_{16}O$ , obtained by reducing isopinole dibromide in glacial acetic acid with zinc dust, has the odour of amylic acetate, boils at  $214-217^{\circ}$ , and has a sp. gr. 0.916 and refractive index  $n_D$  1.46603 at  $20^{\circ}$ . The *semicarbazone* melts at  $158^{\circ}$ , and the *oxime* boils at  $150^{\circ}$  under 15 mm. pressure; reduction of the latter converts it into a base, the *carbamide* derivative of which crystallises from methylic alcohol, and melts at  $186^{\circ}$ .

*Pinolol*,  $C_{10}H_{17}OH$ , prepared from the ketone by reduction in alcohol with sodium, has the odour of linalool, boils at  $108^{\circ}$  under 15 mm. pressure, and has a sp. gr. 0.913, and refractive index  $n_D$  1.47292 at  $20^{\circ}$ .

The derivative of pinole with nitrosyl chloride melts at  $116-120^{\circ}$  when rapidly heated, and is very sparingly soluble in methylic alcohol; the solution in chloroform is colourless at  $-12^{\circ}$ , becoming blue as the temperature rises. The compound in question is pinole *bisnitrosochloride*, which is colourless in the dimolecular form, becoming blue on dissociation.

Pinole *isonitrosochloride*, prepared by passing hydrogen chloride into a solution of the bisnitrosochloride in ethylic acetate, is also produced by the slow, spontaneous change of the dimolecular compound; it dissolves in methylic alcohol, crystallises from ethylic acetate in colourless, transparent prisms, and melts at  $131^{\circ}$ , becoming brown and evolving gas at  $150^{\circ}$ ; the compounds which it yields with bases are identical with those derived from the dimolecular compound.

When the bisnitrosochloride or the isonitrosochloride is heated with an alcohol, chlorine is replaced by hydroxyl. Methylic alcohol yields the compound  $OMe \cdot C_{10}H_{15} \cdot NOH$ , which crystallises in needles and melts at  $138^{\circ}$ ; the compound  $OEt \cdot C_{10}H_{15} \cdot NOH$ , obtained by the action of ethylic alcohol, forms prisms melting at  $100^{\circ}$ . M. O. F.

**Oil of Lemon-Grass.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 77-79).—This essence is mixed with sodium hydrogen sulphite solution, and the crystals of the bisulphite compound obtained are dissolved in water and mixed with barium chloride solution; the barium salt of the citronellal compound is precipitated and the aldehyde regenerated by the action of alcoholic potash; the filtrate from the insoluble citronellal compound is treated with aqueous potash in order to regenerate the citral. The original oil contains 76-77 per cent. of citral, and 7-8 per cent. of citronellal, besides small



quantities of geraniol and methylheptenone (compare Tiemann, Abstr., 1898, i, 677). G. T. M.

**Essential Oils of Lemon-Grass and Citronella.** By JULIEN FLATAU (*Bull. Soc. Chim.*, 1899, [iii], 21, 158—159).—Ziegler's conclusion that the formation of several isomeric semicarbazones proves the existence of various isomerides of citral in oil of lemon-grass is untenable, since carefully purified citral obtained from geraniol yields a mixture of semicarbazones having melting points ranging from 140° to 155°. Oil of lemon-grass consists chiefly of citral, but small quantities of methylheptenone and 2—4 per cent. of citronellal are also present. Oil of citronella contains 25—30 per cent. of citronellal and 2—5 per cent. of citral. N. L.

**Ethereal Salts in Oil of Lemon-Grass.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 159—160).—The high boiling residue previously obtained in the examination of oil of lemon-grass is now shown to consist principally of the ethereal salts of a terpenic alcohol, probably geraniol, with capric and caproic acids which were identified and separated by means of their barium salts. N. L.

**The Three Aldehydes of Oil of Lemon-Grass.** By WILHELM STIEHL (*J. pr. Chem.*, 1899, [ii], 59, 497—516).—The author attributes the differences between his results (this vol., i, 66) and those of Tiemann (*ibid.*, i, 247 and 623) partly to impurities in the latter's material. He upholds the existence of these three aldehydes and attempts to explain their isomerism on stereochemical grounds. R. H. P.

**Isomeric Aldehydes from Oil of Lemon-grass.** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 419—423).—Of the three isomeric semicarbazones prepared by Barbier and the author from oil of lemon-grass (Abstr., 1896, i, 311), that melting at 135° proves to be a mixture of the other two melting at 171° and 164° respectively. These two semicarbazones correspond with Tiemann's citral *a* and citral *b* (this vol., i, 249). T. H. P.

**Constituents of Oil of Petit Grain.** By EUGÈNE CHARABOT and LOUIS PILLET (*Bull. Soc. Chim.*, 1899, [iii], 21, 74—75. Compare this vol., i, 620).—The essence obtained from the leaves and young shoots of *Citrus bigaradia* is hydrolysed and fractionated. The portion distilling below 185° contains no appreciable amount of limonene if care has been taken to exclude the fruit from the raw material. The portion distilling below 197° contains linalool, and this substance forms the chief constituent of the fraction 197—200°; it is separated from geraniol by means of phthalic anhydride and identified by its optical properties and by oxidation to citral. The fraction 220—232° consists chiefly of geraniol which is isolated by means of calcium chloride. The fraction 200—220° contains a mixture of the two alcohols. The hydrolysed oil contains approximately 70—75 per cent. of linalool and 10—15 per cent. of geraniol. The liquid portion of the residue, after distillation, gives the reactions of sesquiterpenes. G. T. M.

**Empyreumatic Oil of Juniper.** By CATHELINEAU and JEAN HAUSER (*Bull. Soc. Chim.*, 1899, [iii], 21, 378—380).—The fraction

extracted by amylic alcohol from that portion of empyreaumatic oil of juniper which is soluble in 5 per cent. aqueous soda (this vol., i, 536) is separated by treatment with hot water into an insoluble, resinous substance, which constitutes from one-third to one-sixth of the whole fraction, and a feebly alkaline solution. The former portion becomes semi-fluid when heated, and is readily soluble in alcohol, chloroform, amylic alcohol, or concentrated acetic acid, but only partially soluble in ether. It is precipitated from its alcoholic solution by normal lead acetate and reduces ammoniacal silver nitrate solution, but has no action on Fehling's solution. Fusion with potash decomposes it into an insoluble resin and a soluble, alkaline portion in which small quantities of resorcinol and pyrogallol were detected.

The alkaline, aqueous solution obtained from the amylic alcohol extract yields, when acidified, a semi-fluid precipitate which is very soluble in alcohol, insoluble in water, ether, or light petroleum. It is precipitated from alcoholic solution by normal lead acetate, reduces ammoniacal silver nitrate solution, but has no action on Fehling's solution. On exposure to air, or on heating with a small quantity of sulphuric acid, it absorbs oxygen and becomes resinous. It is decomposed by heat under ordinary conditions, but by cautious distillation under diminished pressure a phenolic substance was obtained, having an odour of creosote and boiling at 215—250° at the ordinary pressure.

From these results, it is concluded that the amylic alcohol extract of the oil consists for the most part of phenolic ethers of resinous compounds. N. L.

**Tuberone, the Aromatic Principle of the Tuberose Flower.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 306—309).—By distilling in a vacuum a concentrated extract of tuberose, a small quantity of a pure product, boiling at 167° under 15 mm. pressure, is obtained. This substance, which the author calls *tuberone*, possesses in a high degree the odour of the tuberose, which slightly resembles that of coumarin, but is much more fragrant and persistent. It has a sp. gr. 0.9707 at 8°, and a refractive index  $n_D$  1.516 at 14°; it has the formula  $C_{13}H_{20}O$ , which is the same as that of irone obtained from the root of the iris, and is an unsaturated compound, as it decolorises aqueous permanganate, whilst its behaviour with bromine shows that the molecule contains one double linking; probably the constitution may be expressed by the formula,

$$\begin{array}{ccccccc} & & CH_2 \cdot CH_2 & \cdot & CH & \cdot & CO \cdot CH_2 \\ & & | & & | & & | \\ CH_2 \cdot CH_2 & \cdot & CH & \cdot & CH_2 & \cdot & CH \cdot CH_2 \cdot CH : CH_2 \end{array}$$

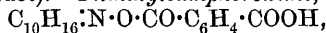
Acetic anhydride has no action on tuberone even on boiling for several hours, but heating with phenylhydrazine causes the elimination of water, indicating the presence of a carbonyl group in the molecule. On heating tuberone with aqueous chromic acid in a reflux apparatus, formaldehyde is produced together with an oily acid which, however, was obtained in quantity insufficient for analysis. T. H. P.

**Derivatives of Camphoroxime.** By GEORGE B. FRANKFORTER and A. D. MAYO (*Amer. Chem. J.*, 1899, 21, 471—473).—The action of acid chlorides and anhydrides on camphoroxime usually leads

to loss of water and formation of campholenic nitrile, but under certain conditions ethereal salts are formed. *Acetylcamphoroxime*,  $C_{10}H_{16} \cdot NOAc$ , prepared by the action of acetic anhydride on camphoroxime in the cold, is a colourless oil of aromatic odour, and boils and decomposes at  $170^{\circ}$ ; it is insoluble in water, but is slowly hydrolysed by it, and is rapidly hydrolysed by sodium hydroxide.

*Chloralcamphoroxime*,  $CCl_3 \cdot CH(\cdot ON : C_{10}H_{16})_2 + 2H_2O$ , prepared by the action of chloral on camphoroxime in cold ethereal solution, separates from alcohol as a fine, white, crystalline, powder, melts at  $82^{\circ}$ , dissolves in ether or alcohol but not in water, and very readily decomposes. *Succinylcamphoroxime*,  $C_{10}H_{16} \cdot NO \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$ , prepared by boiling camphoroxime with succinic anhydride in ethereal solution, is a colourless oil boiling and decomposing at  $246^{\circ}$ , and is hydrolysed by alkalis or by boiling with water. T. M. L.

**Derivatives of Camphoroxime.** By GEORGE B. FRANKFORTER and P. M. GLASOE (*Amer. Chem. J.*, 1899, 21, 474—478. Compare preceding abstract).—*Phthalylcamphoroxime*,



prepared by boiling a solution of camphoroxime in benzene or toluene with an excess of phthalic anhydride, melts at  $135.5^{\circ}$  with decomposition into phthalic acid and campholenic nitrile, and dissolves in ether, alcohol, chloroform, or benzene, but not in carbon bisulphide; it crystallises from dilute alcohol in fine, white needles, but on boiling an alcoholic solution it decomposes slowly into campholenic nitrile and phthalic acid, together with a small quantity of a colourless, odourless oil, which is, perhaps, an ethylic salt of phthalylxime; it is readily hydrolysed by caustic soda.

*Camphorformaldoxime*,  $C_{10}H_{16} \cdot N \cdot O \cdot CH_2OH + H_2O$ , separates in large, white crystals when camphoroxime is heated on a water-bath with formaldehyde and the resulting oil is left covered with water; it melts at  $62$ — $63^{\circ}$ , and can be recrystallised from water, but by strong acids or by boiling the aqueous solution is decomposed into camphoroxime and formaldehyde.

*Camphorparaformaldoxime*,  $C_{10}H_{16} \cdot N(C_3H_5O_3)$ , separates as a thick oil when camphoroxime is heated with an excess of formaldehyde and allowed to remain in a warm place in direct sunlight; when dropped into water containing a little formaldehyde, it passes into the preceding compound.

*Chlorocamphoroxime*,  $C_{10}H_{15}Cl \cdot NOH$ , separates quantitatively in fine needles on adding an ethereal solution of sulphuryl chloride to an ethereal solution of camphoroxime, and melts at  $290^{\circ}$ ; the position of the chlorine atom has not yet been ascertained. T. M. L.

**Opopanax from Umbelliferæ.** By ALEXANDER TSCHIRCH and A. KNITL (*Arch. Pharm.*, 1899, 237, 256—270).—The sample of opopanax examined was the product of the *Opopanax Chironium*, Koch (*Ferula Opopanax*, L.; *Laserpitium Chironium*, L.; *Pastinaca Opop.*, O. orient., Boiss). It was extracted with alcohol, when a gum remained undissolved. By extracting the alcoholic solution, which contained resin, with light petroleum, an essential oil was obtained. After

evaporation of the alcohol, the resin which remained was dissolved in ether; a small portion, possessing the character of a tannol, remained undissolved. By shaking the ethereal solution with a concentrated solution of sodium hydrogen sulphite, vanillin was extracted. By shaking the ethereal solution next with 2—5 per cent. sodium carbonate solution until the former was no longer acid in reaction, ferulic acid was obtained. By boiling the resin with potassium carbonate solution 8 hours a day for 4 months, or by hydrolysing it with sulphuric acid instead, ferulic acid was obtained, but the loss in purification was very great. The alcohol produced simultaneously, *oporesinotannol*, was purified by dissolving it 40 times in alcohol and precipitating it with water acidified with hydrochloric acid, and then digesting it with light petroleum. It is a light brown powder, and has the character of a resinotannol and the composition  $C_{12}H_{13}O_5 \cdot OH$ . It yields a light brown *monobenzoic* derivative when treated by the Schotten-Baumann method, but no acetyl derivative could be obtained. With bromine, it yields a substitution derivative; strong nitric acid converts it on the water-bath into picric and oxalic acids. When dry-distilled, it yields no umbelliferone.

A list of the resinotannols hitherto discovered is given, with their composition, acetyl and benzoyl derivatives, and the products of their oxidation with nitric acid and fusion with potash.

The gum was purified by repeated precipitation with alcohol; it contained 3.53 per cent. of ash, of which 1.67 was calcium and 0.19 magnesium. An arabic acid was prepared from it by dissolving it 40 times in water acidified with hydrochloric acid and precipitating it with alcohol; this contained C 43.17, H 6.42 per cent., a composition which lies between  $C_{12}H_{22}O_{11}$  and  $C_6H_{10}O_5$ . When oxidised with dilute nitric acid on the water-bath, it yields an acid apparently identical with mucic acid. Neither the acid nor the crude gum is optically active. A list is given of the various arabic acids hitherto obtained, with their sources and composition.

By dissolving the essential oil in ether, shaking the mixture with a solution of sodium hydrogen sulphite, and treating the solution with ether, a waxy product was obtained, which, on sublimation, yielded needles which melted at 133—134°, and had the composition C 66.6, H 2.7 per cent.; this substance is named *oponal*.

The resin also contained small quantities of a bitter substance, but this could not be obtained in crystals.

The drug contained, in 100 parts: Resin soluble in ether (oporesinotannol ferulate) 51.8, resin insoluble in ether (free oporesinotannol), 1.90, gum 33.8, essential oil 8.3, free ferulic acid 0.22, vanillin 0.0027, moisture 2.0, bassorin and plant remains 2.0.

The authors have been unable to prepare from galbanum resin the galbanic acid described by Hirschsohn (*Chem. Zeit.*, 1893, 195). A sample of Hirschsohn's acid yielded, on sublimation, crystals which melted at 157—158°, and had the composition  $C_{40}H_{60}O_4$ ; they seem to be identical with, or closely related to, the lævopimaric acid of galipot.

Umbelliferone has been obtained from Sumbul root, but not from *Rad. levistici* or *Mei*.  
C. F. B.

**Cinnamein or Oil of Peru Balsam.** By HERMANN THOMS (*Arch. Pharm.*, 1899, 237, 271—284).—An undoubtedly genuine specimen of Peru balsam, collected personally by a traveller, was previously examined (*Ber. deut. pharm. Ges.*, 1898, 264), and specimens occurring in commerce are now found to have the same constituents. Vanillin can be extracted by shaking an ethereal solution of the balsam with a strong solution of sodium hydrogen sulphite. The ethereal solution can then be hydrolysed with alcoholic potash in the cold; by distilling the product with steam, the alcohols can be driven over, and from the non-volatile residue a substance melting at about 80° and possessing the character of a phytosterol can be isolated. The acids set free on acidifying the residual alkaline solution with hydrochloric acid were shown to consist chiefly of a mixture of benzoic and cinnamic acids, the latter being present to the extent of nearly 40 per cent. The last mother liquors yielded a small quantity of an acid that melted at 79—80°, and appeared to be a *dihydrobenzoic acid*. The mixture of alcohols was fractionated under diminished pressure; benzylic alcohol was obtained as the lower boiling fraction, and a new alcohol, *peruvial*,  $C_{13}H_{22}O$ , in much smaller amount, as a fraction boiling at 139—140° under 7 mm. pressure. This has a sp. gr. 0.886 at 17.5°, and a rotation +13° in a 100 mm. tube; it could not be made to yield an acetyl derivative in a pure state, but a *monocinnamoyl* derivative was obtained when it was heated with cinnamic chloride; it takes up 4Br in acetic acid solution, and so is possibly a hydroaromatic compound with two double linkings in the side chains; when it is oxidised with chromic acid in the cold,  $CH_2$  appears to be replaced by O, which is an argument for the presence of a  $CH_2$  group; when oxidised with alkaline permanganate, at first in the cold, it yields acetic acid together with propionic or possibly butyric acid, and a small quantity of a crystalline acid not volatile with steam.

No iso- or allo-cinnamic acid, or any cinnamylic alcohol (styrone) could be detected in the balsam. C. F. B.

**Composition of Vicin.** By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], 59, 480—481. Compare Abstr., 1881, 1158).—The empirical formula for vicin is  $C_8H_{15}N_3O_6$ , but as vicin yields sugar in appreciable quantity when warmed with dilute sulphuric acid, it is to be regarded as a glucoside, and the molecule must be some multiple of  $(C_8H_{15}N_3O_6)$ ; the author was unable, however, to make a determination of the molecular weight. R. H. P.

**Divicin.** By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], 59, 482—486. Compare Abstr., 1881, 1158).—Further analyses have been made of divicin, and the formula is now given as  $C_4H_7N_4O_2$ . An aqueous solution of divicin possesses strong reducing properties, and is oxidised by strong nitric acid (probably) to allantoin. R. H. P.

**Composition of the Convicins obtained from the Seeds of Vetch and of Vicia Faba.** By HEINRICH RITTHAUSEN and PREUSS (*J. pr. Chem.*, 1899, [ii], 59, 487—488. Compare Abstr., 1881, 1158).—The convicins obtained from these sources proved to be completely identical. Convicin has the composition  $C_{10}H_{15}N_3O_8 + H_2O$ .

R. H. P.

**Capsaicin.** By KARL MICKO (*Chem. Centr.*, 1899, i, 293—294; from *Zeit. Unters. Nahr-Genussm.*, 1898, 818—829).—*Capsaicin*,  $C_{18}H_{28}NO_3$ , prepared from the ethereal extract of the fruit of *Capsicum annum*, which yields 0.03 per cent., crystallises from light petroleum in transparent, colourless plates, melts at 63—63.5°, is easily soluble in ether, alcohol, chloroform, or benzene, rather less so in carbon bisulphide, very slightly in hot water, and insoluble in cold. The crystals easily fall into powder and the dust has an extremely irritating effect on the mucous membrane. An alkaline solution of capsaicin, containing only 0.01 gram in a litre, has a strong burning effect when placed on the tongue. When capsaicin is heated on platinum foil, it emits heavy, violently irritating fumes; it is not volatile in steam, and has the properties of a weak, phenol-like acid. When excess of platinic chloride is added to an alcoholic solution of capsaicin and the mixture allowed to evaporate, after a few hours it acquires the odour of vanillin; even small quantities of capsaicin give this reaction. The molecular weight determined by Beckmann's method in 0.5 per cent. benzene solution was found to be 316, and in 5 per cent. solution 643. The presence of a methoxy-group was proved by Zeisel's method and of a hydroxy-group by the Schotten-Baumann method. The *benzoyl* derivative,  $OMe \cdot C_{17}H_{24}NO \cdot OBz$ , prepared in alkaline solution, crystallises in silky needles and melts at 74°. The determinations of the molecular weight of this compound approached more nearly to the theoretical value.  
E. W. W.

**Compounds from Lichens.** By WILHELM ZOPF (*Annalen*, 1899, 306, 282—321. Compare *Abstr.*, 1895, i, 297; 1896, i, 103; 1897, i, 362, 436; 1898, i, 89, 489).—*Stictaurin*, the orange-red compound obtained from *Sticta aurata* (Ach.), is a derivative of pulvic acid, yielding calycin and ethylpulvic acid under the influence of boiling alcohol; the substance has been obtained from *Candelaria vitellina* (Ehrh.), *C. concolor* (Dicks.), and *Gyalolechia aurella* (Hoffm.), and is probably identical with dipulvic acid, obtained by Hesse from *Candelaria concolor*.

*Caperatic acid*, hitherto isolated by Hesse solely from *Parmelia caperata*, has been obtained by the author from *Platysma glaucum* (L.), and from *Mycoblastus sanguinarius* (L.).

*Lichenostearic acid*, which has been obtained only from Iceland moss (*Cetraria islandica*), occurs also in *Platysma cucullatum* (Bell.); the last-named lichen has yielded usnic acid, which is found also in *Pl. diffusum* (Nyl.), and in *Alectoria ochroleuca* (Ehrh.); the last-named contains barbatic acid.

*Lecanoric acid* occurs in *Psora ostreata*, Hoffm.; *Urceolaria cretacea*, Mass.; *Parmelia tiliacea* var. *scortea*, Ach.; *P. fuliginosa*, Fr., var. *ferruginascens*, Zopf, and *P. verruculifera*, Nyl. With this compound has been identified parmeliatic acid, previously described as occurring in *Urceolaria cretacea*, Mass., and in *Parmelia tiliacea* var. *scortea*, Ach.

*Glomelliferin* is a new compound obtained from *Parmelia glomellifera*, Nyl.; it crystallises from benzene in aggregates of slender needles and melts at 143—144°.

*Atranoric acid* has been already distinguished in forty-five lichens,

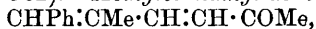
and also occurs in *Platysma glaucum* (L.), Nyl; *Mycoblastus sanguinarius* (L.), and *Parmelia omphalodes* (L.).

*Lecidea sudetica* contains salazinic acid.

*Confluentin*, which crystallises from hot benzene in aggregates of white prisms and melts at 147—148°, is obtained from *Lecidea confluens*, Fr.; *Platysma diffusum* (Web.) yields *diffusin*, which crystallises in silky needles and melts at 135—136°.

Stereocaulic acid occurs in *Stereocaulon pileatum*, Ach., and *Parmelia omphalodes* (L.). M. O. F.

**Conversion of Unsaturated Ketoximes into Pyridine Derivatives. II.** By MAX SCHOLTZ (*Ber.*, 1899, 32, 1935—1939. Compare Abstr., 1895, i, 562).—*Methylcinnamylideneacetone*,



crystallises from alcohol in yellow needles, melts at 62°, and gives a blood-red coloration with concentrated sulphuric acid. The *oxime* crystallises from alcohol in needles, is almost white in colour, and melts at 128°. On dry distillation, it is converted into 2-phenyl-3:6-dimethylpyridine, a pale yellow oil boiling at 286—288° (corr.); the *platinochloride* crystallises in orange-yellow needles and melts at 220°; the *picrate* crystallises in yellow needles and melts at 179—180°.

*Methylcinnamylideneacetophenone*,  $\text{CHPh}:\text{CMe}:\text{CH}:\text{CH}:\text{COPh}$ , crystallises from hot alcohol in glistening, yellow flakes, melts at 81°, and gives a blood-red coloration with concentrated sulphuric acid. The *oxime* crystallises from hot alcohol in pale yellow needles and melts at 165°. On dry distillation, it gives 3-methyl-2:6-diphenylpyridine as a thick, yellow oil boiling at 253—255° under 25 mm. pressure; the *platinochloride* crystallises in orange-yellow needles; the *aurichloride* is precipitated as an oil, but the *mercurichloride*,  $\text{C}_{18}\text{H}_{15}\text{N}, \text{HCl}, 2\text{HgCl}_2$ , crystallises in slender, white needles and melts at 160°. T. M. L.

**Indigotinsubsulphonic Acids.** By B. WILLIAM GERLAND (*J. Soc. Chem. Ind.*, 1899, 18, 225—227).—When indigotin is heated at 100° for a few hours with sulphuric acid of sp. gr. 1·6—1·7, it is completely dissolved; the solution is, however, precipitated by water and the precipitate consists of a mixture of several subsulphonates with a varying amount of monosulphonate.

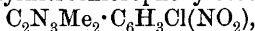
By carefully covering the surface of the acid solution with water and leaving it at rest for a few days, the author succeeded in getting the new substance in a crystalline state; it forms distinct but very fragile needles of a dark, almost black, colour. When the free acid has been removed by washing, it partially redissolves in water, and on adding to this solution calcium acetate or basic lead acetate, barium or ferric chloride, or alum, lakes are obtained, the composition of which is recorded. The compound is also more or less soluble in ethylic or amyl alcohol, acetone, acetic acid, or nitrobenzene.

L. DE K.

**Oxidation of Hydrazoximes. II. and III.** By GIACOMO PONZIO (*Gazzetta*, 1899, 29, i, 277—283; 283—292. Compare Abstr., 1898, i, 386).—*Diacetylparachlorophenylhydrazoxime*,  $\text{NOH}:\text{CMe}:\text{CMe}:\text{N}_2\text{H}:\text{C}_6\text{H}_4\text{Cl}$ , obtained by mixing alcoholic solutions of molecular proportions of

isonitrosomethyl ethyl ketone and parachlorophenylhydrazine, forms yellowish needles melting at  $180-181^{\circ}$ ; it is slightly soluble in cold alcohol, light petroleum, or chloroform, and more so in ether; it does not give Pechmann's reaction with sulphuric acid and ferric chloride.

By gently heating dimethylphenylosotriazole with the theoretical quantity of aqueous chlorine, dimethylparachlorophenylosotriazole,  $C_2N_3Me_2 \cdot C_6H_4Cl$ , is obtained; on treatment with nitric acid, this compound gives dimethylnitrochlorophenylosotriazole,



and with chromic acid it yields methylparachlorophenylosotriazole-carboxylic acid,  $COOH \cdot C_2N_3Me \cdot C_6H_4Cl$ .

*Diacetylorthochlorophenylhydrazoxime*, prepared from isonitrosomethyl ethyl ketone and orthochlorophenylhydrazine, crystallises from chloroform in nearly colourless, flat needles melting at  $189^{\circ}$ , and is slightly soluble in the cold, and more so on heating, in alcohol, chloroform, or benzene; it dissolves in cold ether, but is almost insoluble in light petroleum, and gives Pechmann's reaction.

*Diacetylparabromophenylhydrazoxime*, prepared from isonitrosomethyl ethyl ketone and parabromophenylhydrazine, crystallises from alcohol in lustrous, yellow needles melting at  $195-196^{\circ}$ , dissolves slightly in the cold and more so on heating in alcohol, chloroform, or light petroleum, and shows Pechmann's reaction. With phosphorus pentachloride, it yields *parabromophenyldimethylosotriazole*, melting at  $154-155^{\circ}$ , and by dissolving it in cold fuming nitric acid it is converted into *bromonitrophenyldimethylosotriazole*; the latter melts at  $119-120^{\circ}$ , crystallises from alcohol in lustrous flat needles having a faint yellow colour, and is soluble in cold chloroform or ether.

By heating dimethylphenylosotriazole with the theoretical quantity of iodine and a little water in a sealed tube, dimethylpariodophenylosotriazole is obtained.

*Phenyl-3-methyl-1:2-oxypyrrro-1:4-diazole*,  $O \begin{array}{c} \text{CH} - \text{CMe} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{NPh} \cdot \text{N} \end{array}$ , obtained

by the action of mercuric oxide on methylglyoxalhydrazoxime, forms large, yellowish prisms melting at  $67-67.5^{\circ}$  slightly soluble in hot water and more so in hot light petroleum; in all the other ordinary organic solvents, it is soluble in the cold. It is dissolved by mineral acids and is precipitated unchanged by the addition of an alkali; it is not volatile in steam and decomposes when heated to boiling. On passing dry hydrogen chloride into its ethereal solution, no hydrochloride is formed, but partial conversion into chlorophenylmethylosotriazole takes place; hydrogen iodide under the same conditions yields almost exclusively phenylmethylosotriazole, very little of the iodo-derivative being formed. It is reduced by granulated zinc in concentrated hydrochloric acid solution, yielding phenylmethylosotriazole, and by dissolving in cold concentrated nitric acid, *nitrophenyl-3-methyl-*

*1:2-oxypyrrro-1:4-diazole*,  $O \begin{array}{c} \text{CH} - \text{CMe} = \text{N} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{N}(C_6H_4 \cdot NO_2) \end{array}$  is formed; this crystallises from alcohol in lustrous, yellow needles melting at  $136^{\circ}$ .

*Nitrophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_4 \cdot NO_2$ , prepared by treating phenylmethylosotriazole with concentrated nitric acid, crystal-



lises in thin, yellowish needles melting at 133—134°; it is only slightly soluble in light petroleum, but dissolves in benzene or chloroform even in the cold.

*Amidophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_4 \cdot NH_2$ , obtained by reducing the nitro-derivative in alcoholic solution with zinc and hydrochloric acid, crystallises in almost colourless needles melting at 69°, is slightly soluble in water or light petroleum, and more so in the other organic solvents, and is identical with the compound obtained by reducing the nitro-derivative of phenyl-3-methyl-1:2-oxypyrrro-1:4-diazole. By means of the Sandmeyer reaction, the amido-compound readily yields *chlorophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_4Cl$ , which crystallises in long, thin, lustrous needles melting at 45·5—46° and boiling at 272° under 729 mm. pressure, is volatile in steam and dissolves in the cold in the ordinary organic solvents, but is insoluble in water; it is not oxidised by chromic acid in acetic acid solution, or reduced by hydriodic acid and red phosphorus, but on heating in a sealed tube with dilute hydrochloric acid and potassium dichromate, it is converted into *dichlorophenylmethylosotriazole*,  $C_9H_7N_3Cl_2$ , which crystallises from alcohol in long, glistening needles melting at 117—118°.

*Chloronitrophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_3Cl \cdot NO_2$ , prepared by gently heating chlorophenylmethylosotriazole with nitric acid, crystallises from alcohol in lustrous needles having a very faint yellow tinge, melts at 161—162°, and is soluble in cold chloroform, but only slightly so in cold alcohol, light petroleum, or ether.

*Bromophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_4Br$ , obtained when methylphenylosotriazole is shaken with the theoretical quantity of aqueous bromine, crystallises from alcohol in very thin, lustrous needles melting at 64—65°, is soluble in the ordinary organic solvents, and when heated with bromine and water in a sealed tube at 150°, is converted into *dibromophenylmethylosotriazole*,  $C_9H_7N_3Br_2$ , which separates from alcohol in sparkling laminæ melting at 125—126°.

*Iodophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_4I$ , is formed when phenylmethylosotriazole is heated in presence of water with the theoretical proportions of iodine and iodic acid for several days in a sealed tube at 150°; it crystallises from alcohol in white needles melting at 64—65°, and is soluble in cold ether or benzene, but very slightly so in light petroleum. When heated with nitric acid, it yields *iodonitrophenylmethylosotriazole*,  $C_2N_3HMe \cdot C_6H_3I \cdot NO_2$ , which crystallises from alcohol in long, yellow needles melting at 145—146°, and is soluble in cold ether, but dissolves only slightly in alcohol or light petroleum.

T. H. P.

**Isatin V.** By LEO MARCHLEWSKI and L. G. RADCLIFFE (*Ber.*, 1899, 32, 1869—1872. Compare *Abstr.*, 1895, i, 288; 1896, i, 96, 235, 449).—*Ethoxyindophenazine*,  $\begin{array}{c} C_6H_4 \cdot C:N \\ | \\ NH-C:N \end{array} > C_6H_4 \cdot OEt$ , prepared by the action of parethoxyorthophenylenediamine on isatin, melts at 225°, dissolves in the ordinary organic solvents, and separates from acetic acid or alcohol in yellow crystals.

*Ethoxyorthaminophenimesatin*, 
$$\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{OEt} \\ | \qquad \qquad | \\ \text{N} = \text{C} \cdot \text{OH} \end{array}$$
, pre-

pared by the action of parethoxyorthophenylenediamine on acetyl-pseudoisatin and hydrolysis of the acetate which is first formed, crystallises from alcohol in glistening, yellow needles and melts at 234—235°; it dissolves easily in hot alcohol, ether, or chloroform, gives a yellow solution with caustic alkalis, a brown-yellow solution with concentrated hydrochloric acid, and a red-brown solution with sulphuric acid, the acid solutions becoming cherry-red on adding ether; it is converted into ethoxyindophenazine on heating with acetic acid, and quantitatively by heating with concentrated hydrochloric acid at 140°. Since parethoxyphenylenediamine is not a symmetrical substance, two formulæ are possible for each of the above compounds, and the position of the ethoxy-group has not yet been determined.

T. M. L.

**A New Class of Diazo-compounds. Triazolens.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1773—1797).—When diazoindazole hydroxide (this vol., i, 546) is warmed for a short time with water, it passes over into an anhydride,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C} \cdot \text{N} \cdot \text{N} \\ | \quad \diagdown \quad \diagup \\ \text{N} \quad \text{N} \end{array}$ ,\* which the author calls

*indazoletriazolen*, the four ring system,  $\text{CH}_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{N}$ , being termed a *triazolen* ring. Indazoletriazolen is also formed when the diazohydroxide is shaken with 2N hydrochloric acid and the filtered solution treated with potassium acetate, but it is most readily prepared by the action of nitrous acid on small quantities of amidoindazole; it forms golden yellow needles melting at 105·5—106°, dissolves extremely readily in acetone, acetic acid, chloroform, hot alcohol, or hot water, is only moderately soluble in ether, and sparingly so in light petroleum. When heated for any length of time with water or with light petroleum, it is apt to undergo decomposition. It dissolves with the greatest readiness in dilute mineral acids, forming salts, but is reprecipitated on the addition of acetates. The *hydrochloride*, obtained by passing hydrogen chloride into an ethereal solution of indazoletriazolone, or by diazotising amidoindazole in hydrochloric acid solution, crystallises in yellowish-white, glistening needles, melts and decomposes at 201·5°, and dissolves in water, giving a yellow solution. A solution of the hydrochloride in excess of hydrochloric acid gives a copious scarlet precipitate with bismuth-potassium iodide solution, a greenish-black precipitate with a solution of iodine in potassium iodide, and a white precipitate with phosphotungstic acid. The *platinochloride*,  $(\text{C}_7\text{H}_4\text{N}_4)_2, \text{H}_2\text{PtCl}_6$ , forms a yellowish, glistening precipitate, and only remains constant in weight after being kept for several weeks over sulphuric acid. *Indazole-*

\* In the original, the formula given is  $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \\ | \qquad | \quad | \\ \text{N} \quad \text{N} \quad \text{N} \end{array}$ , and like formulæ are given for the other compounds mentioned. As they are, however, all referred to or derived from indazole, it is to be presumed that the formulæ given in the abstract were intended.

*triazolen-silver nitrate*,  $C_7H_4N_4 \cdot AgNO_3$ , crystallises from water in extremely thin, minute needles, and explodes at  $210-211^\circ$ ; the *mercuri-chloride*,  $C_7H_4N_4 \cdot HgCl_2$ , crystallises in yellowish, micro-crystalline needles and decomposes at  $170-171^\circ$ .

Indazoletriazolen unites very readily with aromatic bases or phenols;

with  $\beta$ -naphthol, a dye,  $N \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{---} \text{NH} \text{---} \end{array} C \cdot N_2 \cdot C_{10}H_6 \cdot OH$ , *indazolylazo- $\beta$ -naphthol* is formed when alcoholic solutions of the constituents are mixed; it crystallises in bright red, glistening needles melting and decomposing at about  $250^\circ$ , dissolves in ethylic or amylic alcohol, and also in hot xylene (see following abstract); it is soluble in 6—7 per cent. sodium hydroxide solution, and the *sodium* derivative may be precipitated by the addition of sodium chloride, but is hydrolysed by much water.

*Indazolylazodimethylaniline*,  $N \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{---} \text{NH} \text{---} \end{array} C \cdot N_2 \cdot C_6H_4 \cdot NMe_2$ , crystal-

lises in dark yellow, glistening needles with a violet lustre, melts at  $256-257^\circ$ , dissolves in concentrated sulphuric acid, and also in  $2N$  hydrochloric acid, yielding the hydrochloride in the form of steel-blue, almost black, needles. Dilute potassium hydroxide decomposes indazoletriazolen, a flocculent potassium derivative being formed. Both water and normal sulphuric acid decompose the triazolen, yielding an amorphous product and indazole. It is also decomposed by concentrated hydrochloric acid when the two are boiled vigorously for some 6 hours, the product formed being chlorindazole (this vol., i, 546). The same product may be obtained by adding copper powder or cuprous chloride to a cold solution of indazoletriazolen in concentrated hydro-

chloric acid. *Iodindazole*,  $C_6H_4 \begin{array}{c} \text{CI} \\ | \\ \text{---} \text{N} \text{---} \end{array} NH$ , is formed when potassium iodide is added to a solution of indazoletriazolen in dilute hydrochloric acid, and is usually accompanied by a considerable quantity of tarry matter; it crystallises from hot, light petroleum in rosettes of glistening needles, melts at  $139-140^\circ$ , and is readily soluble in alcohol, ether, or hot light petroleum.

Boiling hydrobromic acid decomposes indazoletriazolen, yielding a mixture of indazole monobromindazole, dibromindazole, pentabromodi-indazole, 3'-bromindazole(?), an acid and basic substance melting at  $118-119^\circ$ (?), and a strongly acid substance melting at  $213^\circ$ . For the separation of these various products, the original must be consulted.

The monobromindazole,  $C_6H_3Br \begin{array}{c} \text{CH} \\ | \\ \text{---} \text{N} \text{---} \end{array} NH$ , melting at

$124-125^\circ$ , and the dibromindazole,  $C_6H_2Br_2 \begin{array}{c} \text{CH} \\ | \\ \text{---} \text{N} \text{---} \end{array} NH$ , are identical with those described by Fischer and Taefel (Abstr., 1885,

541). Although the latter assign the constitution  $C_6H_3Br \begin{array}{c} \text{CBr} \\ | \\ \text{---} \text{N} \text{---} \end{array} NH$  to their dibromo-derivative, the author considers such a constitution

impossible, since the compound is insoluble in cold dilute sodium

hydroxide. *Pentabromodi-indazole*,  $\text{N} \begin{array}{c} \text{C}_6\text{HBr}_3 \\ \diagup \quad \diagdown \\ \text{---NH---} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{C}_6\text{H}_2\text{Br}_2 \\ \diagup \quad \diagdown \\ \text{---NH---} \end{array} \text{N}$ ,

is soluble in dilute alkali and crystallises from alcohol in colourless, glistening needles melting at  $200\text{--}200.5^\circ$ . The substance described as 3'-bromindazole has not been analysed; it crystallises from hot water in needles melting at  $144^\circ$ , and is soluble in dilute alkali.

When indazoletriazolen hydrochloride is boiled with alcohol, nitrogen is evolved, and indazole is formed, the alcohol being simultaneously oxidised to aldehyde.

1:3-Dimethylindazoletriazolen,  $\text{C}_6\text{H}_2\text{Me}_2 \begin{array}{c} \text{C} \cdot \text{N} : \text{N} \\ | \quad \diagup \quad \diagdown \\ \text{N} \end{array}$ , obtained from 3'-amido-1:3-dimethylindazole (this vol., i, 544), crystallises in long, golden-yellow, glistening needles melting at  $80\text{--}81^\circ$ . During recrystallisation, a small quantity usually decomposes, this decomposition being greater the larger the quantity of material employed. It is readily soluble in most solvents, has a characteristic odour, and gives precipitates with the reagents employed for indazoletriazolen itself.

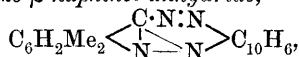
3-Methylindazoletriazolen crystallises in yellow, glistening needles melting at  $104.5\text{--}105.5^\circ$  and is readily soluble in the usual solvents.

J. J. S.

**Anhydro-formation of  $\beta$ -Naphtholazo-dyes.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1797—1802).—When indazoleazo- $\beta$ -naphthol (see preceding abstract) is warmed with amylic alcohol, it loses the elements of water and becomes converted into the *anhydro*-

compound,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C} \cdot \text{N} : \text{N} \\ | \quad \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}_{10}\text{H}_6$ . The reaction is complete after 7 hours boiling, and as the solution cools, golden-yellow, glistening needles of the anhydride are deposited; it melts at  $249^\circ$  without undergoing decomposition, dissolves in concentrated sulphuric or hydrochloric acid, and also in benzene and its homologues, yielding yellowish-green, fluorescent solutions. Other solvents, such as ethylic alcohol, acetic acid, water, chloroform, xylene, cumene, acetone, ether, and light petroleum are also capable of bringing about the anhydro-formation, the amount formed depending both on the temperature and the nature of the medium, hydroxylic compounds, as a rule, being the more active.

*Dimethylindazolylazo- $\beta$ -naphthol anhydride*,



obtained from dimethylindazoleazo- $\beta$ -naphthol (this vol., i, 545) crystallises in orange-yellow, felted needles melting at  $267^\circ$ , and dissolves in concentrated sulphuric acid, yielding a blue-violet solution.

Attempts to convert phenylazo- $\beta$ -naphthol into an anhydride proved unsuccessful.

J. J. S.

**Reduction of Tolualloxazine.** By OTTO KÜHLING (*Ber.*, 1899, 32, 1650—1653. Compare Abstr., 1891, 1342).—By reduction with hydriodic acid, tolualloxazine is converted into *tetrahydrotolualloxazine*,

$C_7H_6 \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \end{smallmatrix}$ , a red, microcrystalline powder which melts above  $300^\circ$ , and is quite insoluble in water, alcohol, ether, or acetone; it dissolves readily in strong acids, but only with difficulty in organic acids; it possesses distinct acidic properties, dissolving in caustic alkalis, alkali carbonates, or in much ammonia, to a yellow solution; an excess of concentrated alkali causes the separation of a white, crystalline salt. The *hydrochloride* separates from concentrated hydrochloric acid in yellow needles.

*Dihydrotolualloxazine*, to which the formula  $C_7H_6 \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CO} \\ \text{N} = \text{C} - \text{CO} - \text{NH} \end{smallmatrix}$  or  $C_7H_6 \begin{smallmatrix} \text{N} = \text{C} \cdot \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \cdot \text{CO} \cdot \text{NH} \end{smallmatrix}$  is assigned, crystallises in minute, yellow needles, and melts and decomposes above  $300^\circ$ ; it dissolves fairly readily in hot water or in alcohol, but not in ether, acetone, or benzene; the aqueous solution is pale yellow, with a blue fluorescence. It does not show basic properties, and is not dissolved by strong acids, but dissolves readily in ammonia, caustic alkalis, and alkali carbonates, giving yellow solutions with a greenish-blue fluorescence. Dilute nitric acid oxidises it to tolualloxazine.

T. M. L.

**Oxazoles.** By MAURICE HANRIOT and G. REYNAUD (*Bull. Soc. Chim.*, 1899, [iii], 21, 14—18).—*Chloroxazolone* is obtained by passing a current of chlorine through amidomethylethylisoxazole immersed in water, distilling the product with steam, and rectifying the distillate under diminished pressure; it boils at  $123^\circ$  under 30 mm. pressure, and, when heated with hydrochloric acid, yields  $\alpha$ -chlorodiethyl ketone. Bromoxazolone, when treated in this way, gives rise to a mixture of  $\alpha$ -chloro- and  $\alpha$ -bromo-diethyl ketones.

When bromoxazolone is dissolved in cold potash, the bromine is eliminated, and a viscid product is formed; this substance decomposes at  $30^\circ$ , evolving carbonic anhydride; it appears to be the *oxime* of  $\alpha\alpha$ -propionylhydroxypropionic acid; its *barium* salt,  $BaC_{12}H_{20}N_2O_8$ , and *silver* salt,  $AgC_6H_{10}NO_4 + H_2O$ , have been analysed. Since the oxime is monobasic, it is probably an anhydride, having the constitution

tion  $\begin{smallmatrix} \text{C}^{\text{Et}} \\ \text{N} \cdot \text{O} \end{smallmatrix} > \text{CMe} \cdot \text{COOK}$ . When the free acid is allowed to decompose spontaneously, a viscid liquid is obtained, which cannot be distilled even in a vacuum; it appears to be identical with the condensation product obtained from  $\alpha$ -chlorodiethyl ketone and hydroxylamine, for both substances, when boiled with hydrochloric acid, are hydrolysed into methyl ethyl diketone (acetylpropionyl), hydroxylamine, and ammonia, and a small amount of the nitroso ketone,  $\text{COME} \cdot \text{CET} \cdot \text{NOH}$ . When bromoxazolone is heated with a solution of caustic potash or potassium carbonate, the chief product of the reaction is a substance melting at  $182^\circ$ ; it is accompanied by another *compound* melting at  $137^\circ$ , and a small quantity of methyl ethyl diketone. The substance melting at  $182^\circ$  is also produced by the action of mercury or sodium amalgam on bromoxazolone, and from its mode of formation it should

have the constitution  $\text{N} \begin{smallmatrix} \text{O} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CEt} \end{smallmatrix} \text{CMe} \cdot \text{CMe} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagdown \quad \diagup \\ \text{CEt} \end{smallmatrix} \text{N}$ . The compound melting at  $137^\circ$  has the composition  $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_3$ , and may be regarded as the condensation product of the anhydride of the oxime of methylethylketole with that of methylethylketolecarboxylic acid.

G. T. M.

**Dionine, a new Morphine Derivative.** By LUDWIG HESSE (*Chem. Centr.*, 1899 i, 430—431; from *Pharm. Centr.-H.*, 40, 1—5).—*Ethylmorphine hydrochloride* or *dionine*,  $\text{OH} \cdot \text{C}_{17}\text{H}_{17}\text{NO} \cdot \text{OEt} \cdot \text{HCl} + \text{H}_2\text{O}$ , is a white, odourless, finely crystalline powder, has a bitter taste, melts at  $123$ — $125^\circ$ , dissolves easily in water, forming a neutral solution, is very slightly soluble in alcohol, insoluble in ether or chloroform, and is precipitated even from dilute aqueous solutions by most alkaloidal reagents. It can scarcely be distinguished from codeine by its colour reactions, but whilst codeine is precipitated from 5 c.c. of a 10 per cent. solution of its hydrochloride by adding a few drops of ammonia solution of sp. gr. 0.91, and is permanently dissolved when 1 c.c. of ammonia is added, ethylmorphine when precipitated in a similar manner is only dissolved by 5 c.c. of ammonia, and the solution after a short time deposits crystals which melt at  $93^\circ$ ; this precipitation is evident, even in solutions containing only 1 per cent. Ethylmorphine may be distinguished from morphine by the bluish-green coloration formed when 1 c.c. of a 1 per cent. aqueous solution is treated with a solution of a granule of potassium ferrocyanide in 10 c.c. of water containing a drop of a ferric chloride solution; morphine under similar conditions gives a dark blue coloration. Ethylmorphine hydrochloride is used as an anodyne and narcotic.

E. W. W.

**Solubility of Proteids in Glycerol.** By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], 59, 479—480).—An historical review.

R. H. P.

**Proteids of Wheat-Gluten.** By HEINRICH RITTHAUSEN (*J. pr. Chem.*, 1899, [ii], 59, 474—478).—An historical review of the subject and a criticism of Morishima's work (this vol., i, 466).

R. H. P.

**A Slow Proteid Decomposition.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, 27, 305—316).—Fibrin was infected with putrefactive bacteria, and kept in chloroform water; it remained sterile for months and even years, but nevertheless underwent solution, proteoses, peptone, and, finally, leucine and tyrosine being formed. This change is believed to be due to an enzyme secreted by the bacteria. Among other points of interest noted, is that a reducing sugar was split off from the proteid during this process.

W. D. H.

**Influence of Carbohydrates on the Putrefaction of Proteids.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, 27, 316—319).—Blood saturated with cane sugar underwent no putrefaction. There was, however, a growth of moulds, which, acting on the sugar, produced alcohol, acetic acid, and ethylic acetate; the hæmoglobin was consequently changed into acid hæmatin.

W. D. H.

## Organic Chemistry.

**Action of Chlorine on Propylic Chloride in presence of Anhydrous Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1899, [iii], 21, 616—623).—By gradually adding anhydrous aluminium chloride to dry propylic chloride kept at 0°, and subsequently heating the liquid to 30—35°, large volumes of hydrogen chloride are set free and propylene is formed. This affords a probable explanation of the production of isopropylbenzene when propylic chloride and benzene react in presence of aluminium chloride; the propylic chloride decomposes into propylene and hydrogen chloride, isopropylic chloride being formed by the recombination of these products.

If a brisk current of chlorine is passed through the propylic chloride at 0° to which aluminium chloride is being gradually added, propylenic dichloride is obtained.

On chlorinating propylenic dichloride at 35—40°, aluminium chloride being added little by little, the principal product is  $\alpha\alpha\beta$ -trichloropropane, small quantities of other chloropropanes and of trichlorhydrin being also formed.

When  $\alpha\alpha\beta$ -trichloropropane is further chlorinated at 80—85° in presence of aluminium chloride,  $\alpha\alpha\beta\gamma$ -tetrachloropropane and a pentachloropropane which boils at 194—196° and has a sp. gr. 1·614 at 16°, are obtained.

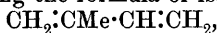
T. H. P.

**Chlorobromo-derivatives containing Two Atoms of Carbon.** By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1899, i, 588; from *Bull. Acad. roy. Belg.*, 1898, [iii], 36, 519—531).—By the action of antimony pentachloride on tribromethylene dissolved in carbon tetrachloride,  $\alpha\beta$ -dichloro- $\alpha\alpha\beta$ -tribromethane, chlorotetrabromethane, and chlorotribromethylene are formed.  $\alpha\beta$ -Dichloro- $\alpha\alpha\beta$ -tribromethane is a colourless liquid, boils at 133° under 35 mm. pressure, boils and decomposes at 210° under the ordinary pressure, solidifies at -5°, has a sp. gr. 2·6263 at 21·5° and a specific refractive index 1·5989 at 15·5°. When boiled with alcoholic potash, it yields  $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromethylene, which is a colourless liquid with a pleasant odour, boils at 172° under 765 mm. pressure, solidifies below 0°, has a sp. gr. 2·3753 at 17·5°, a specific refractive index 1·5800 at 16°, and is not attacked by concentrated sulphuric acid. By passing the vapour of  $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromethylene with carbonic anhydride through a red-hot tube, perchlorobenzene, bromine, and chlorine are formed.  $\alpha\beta$ -Dichloro- $\alpha\alpha\beta\beta$ -tetrabromethane, prepared by the action of bromine on dichlorodibromethylene dissolved in chloroform, forms large crystals, is soluble in chloroform or benzene, slightly so in alcohol or ether, gives off bromine at 140° and melts at 191°.  $\alpha\beta$ -Dichloro- $\alpha$ -bromethylene, obtained by reducing dichlorotribromethane with zinc dust and alcohol, boils at 112—113°, does not solidify at -20°, has a sp. gr. 1·8764 at 17·5°, a specific refractive index 1·5190 at 16°, and readily combines with bromine to form dichlorotribromethane. From these reactions, the formula of dichloro-

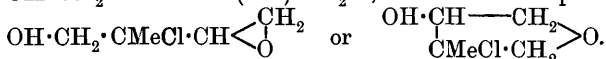
tribromethane is probably  $\text{CClBr}_2 \cdot \text{CHBrCl}$ , the antimony pentachloride apparently not affecting the position of the bromine atom as it does in the case of dibromethylene. E. W. W.

**Isoprene.** By WLADIMIR MOKIEWSKY (*Chem. Centr.*, 1899, i, 589—591; from *J. Russ. Chem. Soc.*, 1898, 30, 885—900).—Isoprene is most cheaply prepared from turpentine by Tilden's method (*Trans.*, 45, 413), which yields 1.5—3 per cent. The crude product cannot be purified by fractionating, and towards the end of the distillation it explodes violently; it boils at 30—40°, readily chars, and contains about 50 per cent. of isoprene, the remainder consisting mainly of trimethylethylene. The latter compound has also been found in the isoprene from caoutchouc (Ipatieff and Wittorf, *Abstr.*, 1897, i, 233), and its derivatives were probably confused with amylene derivatives by Berkenheim (*J. Russ. Chem. Soc.*, 1895, 27, 183), and Bouchardat (*Abstr.*, 1880, 323). According to Faworsky, the combination of isoprene with hypochlorous acid can be used to determine the structure of unsaturated compounds,  $\text{C}_n\text{H}_{2n-2}$ , and the formation of a dichlorhydrin of isoprene-erythritol,  $\text{C}_5\text{H}_8\text{Cl}_2(\text{OH})_2$ , would indicate the presence of a double linking in isoprene.

By the action of a cold, dilute solution of hypochlorous acid on isoprene, a yellowish-brown, viscous liquid is obtained, from which the *chlorhydrin* of trimethylene glycol,  $\text{C}_5\text{H}_{11}\text{ClO}$ , and the *chlorhydrin* of isoprene-erythritol were isolated. The former boils at 141°, has a sp. gr. 1.0562 at 0°/0°, 1.0355 at 22°/22°, and yields an oxide and glycol identical with trimethylene oxide and Eltekoff's glycol respectively. The latter crystallises from alcohol, ether, or benzene, melts at 82.5°, and when heated with water at 120° forms a compound,  $\text{C}_5\text{H}_9\text{Cl} \cdot \text{OH}$ , which melts at 72.5—73°, sublimes readily, and is easily soluble in water or ether. Assuming the formula of isoprene to be



and that of the chlorhydrin to be  $\text{OH} \cdot \text{CH}_2 \cdot \text{CMeCl} \cdot \text{CHCl} \cdot \text{CH}_2 \cdot \text{OH}$  or  $\text{OH} \cdot \text{CH}_2 \cdot \text{CMeCl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$ , then this compound is probably



Attempts to obtain the erythritol compound from the ethylic salt of the chlorhydrin also failed. The mother liquor of the chlorhydrin yielded a fraction boiling at 130—160° under 20 mm. pressure, and the residue formed a syrup which boiled at 135—143°. From the former, a small quantity of a crystalline compound was obtained, but even after repeated distillation it contained 41.9 per cent. of chlorine, whilst the amount required for an isomeride of  $\text{C}_5\text{H}_8\text{Cl}_2(\text{OH})_2$  is only 41.0 per cent.

By the action of bromine (1 mol.) on a cooled ethereal solution of isoprene, hydrogen bromide is evolved and 65 per cent. of an almost colourless product obtained, which, when distilled, yields two fractions, one boiling at 60—64°, and the other at 90—94°, under 12 mm. pressure. By the action of zinc dust on the former, a hydrocarbon boiling at 36—38° is formed, and this, when dissolved in sulphuric acid and precipitated by potassium carbonate by Wyszchnegradsky's method, yields amylic alcohol. Hence Berkenheim's second isoprene



dibromide is really an amylene derivative. The second fraction consists of *isoprene dibromide*,  $\text{CMeBr} \begin{smallmatrix} \text{CH}_2 \\ \text{CHBr} \end{smallmatrix} \text{CH}_2$ ; it is a very unstable liquid, has a penetrating odour, and easily chars. When treated with zinc dust, it yields 70 per cent. of pure isoprene, which is very unstable, boils at  $33.5^\circ$ , and has a sp. gr. 0.6989 at  $0^\circ/0^\circ$  and 0.6794 at  $19^\circ/0^\circ$ . Isoprene dibromide combines with bromine only with difficulty, and when treated with bromine (1 mol.) forms the tetrabromide,  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , but some hydrogen bromide is always liberated. The corresponding *glycol (dibromhydrin)*,  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$  or  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , prepared by oxidising the dibromide with a 1 per cent. solution of potassium permanganate by Wagner's method, crystallises from hot ether in long, colourless prisms, is odourless, melts at  $126.5^\circ$ , sublimes when heated above the melting point, and by the action of zinc dust is converted into a hydrocarbon. Attempts to prepare the erythritol compound from this glycol resulted only in the formation of substances containing bromine.

The use of hypobromous acid, instead of hypochlorous acid is recommended, on account of its easier preparation and the better yields obtained. The liquid obtained by the action of bromine on mercuric oxide is employed, and the product of the reaction is treated with a small excess of potassium sulphide and filtered. The *isoprene dibromhydrin*,  $\text{C}_5\text{H}_8\text{Br}_2(\text{OH})_2$ , obtained by treating isoprene with hypobromous acid, crystallises in hexagonal plates and melts at  $86^\circ$ . E. W. W.

**A New Hexavalent Hydrocarbon, 2-Methyl-3-hexene-5-ine.** By VICTOR GRIGNARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 574—575).—By the action of phosphorus pentachloride on 2:3:5-methylhexenone, a mixture of a mono- and a di-chloro-derivative,  $\text{C}_7\text{H}_{11}\text{Cl}$  and  $\text{C}_7\text{H}_{12}\text{Cl}_2$ , is obtained. By acting on these two separately with potash and distilling the products at 80 mm. pressure, the fractions passing over below  $80^\circ$ , which possess the alliaceous odour of the acetylene hydrocarbons, give, when mixed and redistilled, a principal fraction boiling at  $117\text{—}120^\circ$  under 750 mm. pressure; it contains a little chlorine, but consists essentially of *2-methyl-3-hexene-5-ine*,  $\text{CHMe}_2\cdot\text{CH}:\text{CH}\cdot\text{C}:\text{CH}$ . With ammoniacal cuprous chloride, it gives beautiful, bright yellow flocks of a *copper* compound,  $(\text{C}_7\text{H}_9)_2\text{Cu}_2 + \text{H}_2\text{O}$ , which deflagrates violently when heated or when treated with a few drops of concentrated nitric acid; with Béhal's reagent (saturated alcoholic silver nitrate) it forms thin, white spangles of a *silver* compound,  $\text{C}_7\text{H}_9\text{Ag}\cdot\text{AgNO}_3$ , which detonates on heating and is slightly soluble in alcohol. T. H. P.

**2-Methyl-4-heptene-6-ine and 2-Methyl-4:5:6-heptatriene.** By VICTOR GRIGNARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 576—578).—On treating methylheptenone with phosphorus pentachloride, the principal products are two isomerides of the composition  $\text{C}_8\text{H}_{13}\text{Cl}$ , which, under 10 mm. pressure, boil at  $72\text{—}75^\circ$  and  $80^\circ$  respectively. On treating these with potash and purifying, *2-methyl-4-heptene-6-ine*,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{C}:\text{CH}$ , is obtained as a liquid boiling at  $126\text{—}129^\circ$  under 750 mm. pressure

and having a strong alliaceous odour. The addition of ammoniacal cuprous chloride solution precipitates a bright yellow *copper* compound,  $(C_8H_{11})_2Cu_2 + H_2O$ , which deflagrates violently on heating or on treating with a little concentrated nitric acid. The *silver* compound,  $C_8H_{11}Ag, AgNO_3$ , obtained by the action of Béhal's reagent, forms nacreous scales which dissolve slightly in alcohol, turn yellow on exposure to light, and detonate on heating.

From a higher boiling fraction of the products of the action of potash on the two chloro-compounds,  $C_8H_{13}Cl$ , 2-methyl-4:5:6-heptatriene,  $CHMe_2 \cdot CH_2 \cdot CH:C:C:CH_2$ , is obtained as a liquid boiling at 79—82° under 80 mm. pressure and having a strong alliaceous odour more disagreeable than that of its isomeride, 2-methyl-4-heptene-6-ine. It gives no precipitate either with ammoniacal cuprous chloride solution or with Béhal's reagent, but in aqueous alcoholic solution, mercuric chloride gradually forms a white precipitate. When heated with potassium under pressure, the *potassium* derivative is obtained, and this, with Béhal's reagent, gives a precipitate of the *silver* compound,  $C_8H_{11}Ag, AgNO_3$ .

T. H. P.

**Theory of the Action of Carbonic Oxide on a Solution of Potassium Ferrocyanide.** By JOSEPH AUGUSTE MULLER (*Bull. Soc. Chim.*, 1899, [iii], 21, 472—475).—Carbonic oxide acts on a solution of potassium ferrocyanide according to the equation  $K_4FeC_6N_6 + CO + 2H_2O = K_3(CO)FeC_5N_5 + NH_3 + HCOOK$  (see Abstr., 1898, i, 615). The yield increases when an excess of carbonic oxide is used. The reaction, however, is not reversible; the mass action of the carbonic oxide is explained by the fact that it prevents the occurrence of the secondary reaction  $4K_3(CO)FeC_5N_5 + 4H_2O = 3K_4FeC_6N_6 + 4CO + (HCOO)_2Fe + 2NH_3$ .

R. H. P.

**Regeneration of Denatured Alcohol by means of Bleaching Powder.** By A. and P. BUISINE (*Bull. Soc. Chim.*, 1899, [iii], 21, 446—448).—A reply to Duchemin (this vol., i, 666), who states that spirits denatured by the addition of methyl ethyl ketone can be readily recovered by means of bleaching powder. The authors point out that, in 1896, Arachequesne proposed this method of regeneration for ordinary methylated spirits, but it has never been employed. They state also that when it is used with spirits containing methyl ethyl ketone, there is great difficulty in removing all the chloroform formed, and further, the alcohol obtained has a very bad flavour which cannot be got rid of, whilst the presence of chlorine compounds yielding hydrogen chloride, on combustion, prevents its use for burning or lighting.

T. H. P.

**Derivatives of Nitroethanol [Nitroethylic Alcohol].** By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 255—266).— $\beta$ -Nitroethylic alcohol (Abstr., 1898, i, 505) has at the same time the character of an alcohol and of a nitro-compound. As an alcohol, when treated with phosphorus pentachloride, it yields  $\alpha\beta$ -chloronitroethane,  $NO_2 \cdot CH_2 \cdot CH_2Cl$  (*loc. cit.*), which will not condense with formaldehyde, and, when warmed with hydrochloric acid, is decomposed into hydroxylamine hydrochloride and chloracetic acid. It also yields

an *acetate*,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OAc}$ , which boils at  $118-119^\circ$  under 30—35 mm. pressure, and has a sp. gr. 1.2132 at  $11^\circ$ . *Nitroethylic ether*,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OEt}$ , can be prepared by heating iodoethylic ether,  $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{OEt}$ , with silver nitrate; it boils at  $178^\circ$  under 760 mm. pressure, and has a sp. gr. 1.148 at  $16^\circ$ . It cannot, however, be oxidised to nitroacetaldehyde or nitroacetic acid by means of dichromate and sulphuric acid.

As a nitro-compound, it is found to unite with formaldehyde (in 40 per cent. solution) under the influence of a fragment of potassium carbonate; the product is tertiary nitrotrihydroxybutane (Abstr., 1896, i, 4). With a mixture of piperidine in formaldehyde solution, in which the compound  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_{10}$  is present, it reacts, forming a *compound*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}(\text{NO}_2)(\text{CH}_2 \cdot \text{C}_5\text{NH}_{10})_2$ , which melts at  $94-95^\circ$ . By adding to its ethereal solution either alcoholic sodium ethoxide or metallic sodium, a *sodium* derivative,  $\text{NO}_2 \cdot \text{CHNa} \cdot \text{CH}_2 \cdot \text{OH}$ , can be precipitated.

When nitromethylisopropylcarbinol,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CHMe}_2$  (Abstr., 1898, i, 4) is mixed with a 40 per cent. solution of formaldehyde, and some fragments of potassium carbonate are added, a *compound*,  $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{NO}_2)(\text{CH}_2 \cdot \text{OH})_2$ , is formed; this melts at  $103-104^\circ$ .  
C. F. B.

**Action of Zinc Dust on Bromalcohols.** By WLADIMIR MOKIEWSKY (*Chem. Centr.*, 1899, i, 591—592; from *J. Russ. Chem. Soc.*, 1898, 30, 900—903).—When hydrogen bromide is passed into ethylene glycol according to Henry's method (*Ann. Chim. Phys.*, 1872, [iv], 27, 250), only half the quantity required to form bromethylic alcohol can be used, owing to the crystallisation of the whole mass. When the product is heated, and the gas again passed in, only ethylenic bromide is formed. Henry's ethylene glycol was probably impure. A 60 per cent. yield of bromethylic alcohol is obtained by the action of hypobromous acid (this vol., p. 727) on ethylene. By the action of zinc dust (Gustavson and Demjanoff, *J. Russ. Chem. Soc.*, 20, 615) on bromethylic alcohol, ethylene is formed. A 65 per cent. yield of *bromamylic alcohol* is obtained by the action of hypobromous acid on trimethylethylene; this alcohol boils at  $45-46^\circ$  under 12 mm. pressure, has a sp. gr. 1.4104 at  $0^\circ/0^\circ$ , 1.3821 at  $21^\circ/0^\circ$ , and when treated with zinc dust, yields trimethylethylene.  
E. W. W.

**Action of Hydrogen Bromide on Glycols.** By WLADIMIR MOKIEWSKY (*Chem. Centr.*, 1899, i, 592; from *J. Russ. Chem. Soc.*, 1898, 30, 904—906).—The crystalline mass obtained by passing hydrogen bromide into ethylene glycol (see preceding abstract) is an additive *compound*,  $\text{C}_2\text{H}_4(\text{OH})_2 + \text{HBr}$ ; it is stable only in an atmosphere of hydrogen bromide, and melts at  $50-51^\circ$ . The corresponding *compound*,  $\text{C}_3\text{H}_6(\text{OH})_2 + \text{HBr}$ , prepared from trimethylene glycol, melts at  $209-210^\circ$ . When hydrogen bromide is passed into trimethylethylene glycol, more hydrogen bromide is used than is necessary for the formation of a similar additive compound, there is no separation of crystals, and the product consists of two layers.  
E. W. W.

Preparation of the Higher Aliphatic Amines; Undecylamine and Pentadecylamine. By ELIZABETH JEFFREYS (*Amer. Chem. J.*, 1899, 22, 14—44).—Hofmann's method of preparing aliphatic amines from acid amides does not yield good results in the case of the higher amines, owing to secondary changes occurring, which give rise to aliphatic nitriles and mixed acyl-alkylic carbamides of the type  $\text{RNH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{R}$ . The author finds, however, that when bromine is added to a solution of sodium methoxide and any acid amide in methylic alcohol, an aliphatic urethane is formed according to the equation  $\text{RCO}\cdot\text{NH}_2 + \text{Br}_2 + 2\text{NaOMe} = \text{RNH}\cdot\text{COOMe} + 2\text{NaBr} + \text{MeOH}$  (compare Lengfeld and Stieglitz, *Abstr.*, 1893, i, 310 and 631; 1894, i, 415); on distilling the urethane so obtained with lime, an excellent yield of the corresponding amine is obtained. In order that the best yield of urethane should be obtained by this method, it is necessary to mix the substances together as rapidly as possible; if the sodium methoxide solution is added gradually to the solution of the amide and bromine, or if the bromine is added drop by drop to the mixture of the amide and the methoxide, a large proportion of a mixed carbamide is formed according to the equation  $\text{RCO}\cdot\text{NHBr} + \text{RCO}\cdot\text{NH}_2 + \text{NaOMe} = \text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHR} + \text{NaBr} + \text{MeOH}$ . The formation of mixed carbamides, when the higher amides are submitted to Hofmann's method, is therefore undoubtedly due to the fact that their low solubility in aqueous alkali causes the molecular rearrangement of the acid amide to take place so slowly that the latter is always present in excess.

It is usually assumed that isocyanates are, under ordinary conditions, intermediate products of the Beckmann transformation; that they are not formed in the rearrangement of acid bromamides in presence of alkali or sodium methoxide appears probable since benzamide, interacting with phenylic isocyanate dissolved in methylic alcohol, invariably gives rise to phenylmethylethane, without yielding a trace of benzophenylcarbamide. Hoogewerff and van Dorp assumed that bromoformamides are the first products of the same transformation, but since chloroformanilide interacting with benzamide yields hardly a trace of benzophenylcarbamide, their view appears to be discredited.

The new method of preparing urethanes from acid amides is applicable in the case of aromatic amides, but fails with unsaturated compounds of the type  $\text{RCH}:\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , owing to the unsaturated group entering into action.

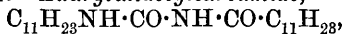
Further details are given as to palmitic chloramide, methylic pentadecylcarbamate, pentadecylcarbamide, and normal pentadecylamine (*Abstr.*, 1897, i, 315); the hydrochloride of the last crystallises in glistening leaflets and decomposes without melting at  $200^\circ$ , whilst the platinochloride decomposes at  $205^\circ$ .

*Pentadecylamine pentadecyldithiocarbamate* melts at  $99^\circ$ , and, on heating for 20 hours at  $100^\circ$ , is converted into *dipentadecylthiocarbamide*,  $(\text{C}_{15}\text{H}_{31}\cdot\text{NH})_2\text{CS}$ , which melts at  $88.5^\circ$ . *Pentadecylthiocarbimide*,  $\text{C}_{15}\text{H}_{31}\cdot\text{NCS}$ , is formed on heating pentadecylamine dissolved in absolute alcohol with an excess of carbon bisulphide during 2

days; *phenylpentadecylthiocarbamide*,  $C_{22}H_{38}N_2S$ , prepared from it, crystallises from alcohol and melts at  $79^\circ$ . *Pentadecylcarbamic chloride*,  $C_{15}H_{31}NH \cdot COCl$ , prepared by heating pentadecylamine hydrochloride with liquid phosgene for 10 hours at  $100^\circ$ , is comparatively stable, and loses hydrogen chloride only slowly when heated at  $150^\circ$  in a stream of air. *Pentadecylic isocyanate*,  $C_{15}H_{31}NCO$ , melts at  $8-14^\circ$ , *pentadecylphenylcarbamide*,  $C_{22}H_{38}N_2O$ , at  $94^\circ$ , whilst *dipentadecylcarbamide*,  $(C_{15}H_{31} \cdot NH)_2CO$ , crystallises from alcohol in small needles and melts at  $113^\circ$ . Pentadecylic alcohol melting at  $45-46^\circ$ , is formed on treating pentadecylamine hydrochloride with boiling aqueous sodium nitrite; the principal product of this action, however, appears to be the hydrocarbon  $C_{15}H_{30}$ . *Pentadecylic phenylcarbamate*, prepared from the alcohol and phenylic isocyanate, crystallises from light petroleum in leaflets, melts at  $72^\circ$ , and serves as a means of characterising pentadecylic alcohol.

*Methylic heptadecylcarbamate*,  $C_{17}H_{35} \cdot NH \cdot COOMe$ , prepared from stearamide, crystallises from light petroleum or alcohol in leaflets, melts at  $63-64^\circ$ , and is converted almost quantitatively into heptadecylamine (Turpin, Abstr., 1888, 1174) when distilled with lime.

*Methylic undecylcarbamate*,  $C_{11}H_{23} \cdot NH \cdot COOMe$ , prepared from lauramide, melts at  $45-47^\circ$ , and can be distilled unchanged under diminished pressure. *Laurylundecylcarbamide*,



is formed by the action of bromine and sodium methoxide on lauramide, unless the reagents are rapidly brought together; it crystallises from alcohol in leaflets and melts at  $105^\circ$ . *Normal undecylamine*,  $C_{11}H_{23} \cdot NH_2$ , melts at  $15^\circ$ , boils at  $232^\circ$  under 742 mm. pressure, and rapidly absorbs water and carbonic anhydride from the air; the *hydrochloride*,  $C_{11}H_{25}N \cdot HCl$ , crystallises in lustrous plates and decomposes without melting, and the *platinochloride*,  $(C_{11}H_{25}N)_2 \cdot H_2PtCl_6$ , behaves similarly; the *benzoyl* derivative,  $C_{11}H_{23} \cdot NHBz$ , crystallises in needles and melts at  $60^\circ$ , whilst *undecylcarbamide*,  $C_{11}H_{23}NH \cdot CO \cdot NH_2$ , crystallises from alcohol in prisms and melts at  $110^\circ$ . The action of nitrous acid on normal undecylamine gives rise principally (compare Victor Meyer and Forster, Abstr., 1876, ii, 182; 1877, ii, 285) to an *undecylene*,  $C_{11}H_{22}$ , which boils at  $84^\circ$  under 18 mm. pressure, and yields a *dibromide*,  $C_{11}H_{22}Br_2$ , boiling at  $161^\circ$  under the same pressure; only a small quantity of *normal undecylic alcohol*,  $C_{11}H_{23} \cdot OH$ , is formed, and this melts at  $19^\circ$ , boils at  $131^\circ$  under 15 mm. pressure, and yields undecic acid on oxidation with potassium dichromate; *normal undecylic phenylcarbamate*,  $C_6H_5 \cdot NH \cdot COO \cdot C_{11}H_{23}$ , crystallises from alcohol in needles and melts at  $62^\circ$ .

*Ethylic pentadecylcarbamate*,  $C_{15}H_{31} \cdot NH \cdot COOEt$ , prepared by the interaction of sodium ethoxide, bromine, and palmitamide in alcoholic solution, melts at  $54^\circ$  and boils at  $225^\circ$  under 14 mm. pressure.

The action of sodium methoxide and bromine on cinnamide dissolved in methylic alcohol gives rise to a *substance*,  $C_{10}H_{12}NO_2Br$ , which melts and decomposes at  $218^\circ$ , and possibly has the structure

CHPhBr·CH(OMe)·CO·NH<sub>2</sub>; salicylamide gives rise under the same conditions to dibromosalicylamide (compare McCoy, this vol., i, 359).

W. A. D.

**Free Chitosamine.** By C. A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 77—85. Compare this vol., i, 5, and Breuer, *Abstr.*, 1898, i, 620).—Free chitosamine (glucosamine) is prepared by mixing the hydrochloride with 10—15 times its weight of pure methylic alcohol containing a little more than the calculated quantity of sodium ethoxide. After a quarter of an hour, the solution is filtered from the precipitated sodium chloride; chitosamine, C<sub>6</sub>H<sub>13</sub>NO<sub>5</sub>, is then deposited, and may be recrystallised from methylic alcohol. Instead of the sodium methoxide, sodium acetate and even sodium nitrite may be used. Chitosamine melts at 105—110°, and has a specific rotation  $[\alpha]_D + 44^\circ$  in 0.4 per cent. aqueous solution. In 1 per cent. aqueous solution it is stable, but in 9 per cent. solution it decomposes slowly; it also decomposes in methyl-alcoholic solution, slowly at the ordinary temperature, but more quickly if kept at 32° or boiled for a short time. One product of the decomposition is the ammoniacal derivative of fructose (next abstract but one); others are amido-derivatives of carbohydrates, and from these a mixture of two osazones was prepared which could be separated with alcohol; one of these was *d*-glucosazone.

From chitosamine hydrochloride a mixture of two *pentacetyl* derivatives of chitosamine can be prepared; of these, the less soluble in 50 per cent. alcohol ( $\alpha$ -compound) melts at 183.5° and is optically inactive, whilst the more soluble ( $\beta$ ) melts at 133° and has a specific rotation  $[\alpha]_D + 86.5^\circ$  in 2 per cent. chloroform solution. C. F. B.

**A Derivative of *d*-Glucosamine.** By B. SJOLLEMA (*Rec. Trav. Chim.*, 1899, 18, 292—295).—After *d*-glucosamine (Lobry de Bruyn, *Abstr.*, 1895, i, 640) has been boiled for several hours with absolute methylic alcohol, ether precipitates from the solution a hygroscopic substance; this, when washed with moist ether, forms a thick syrup from which crystals deposit when it is allowed to remain. These melt at 132—134°, and have the composition C<sub>12</sub>H<sub>23</sub>NO<sub>10</sub> + 2H<sub>2</sub>O; their rotation in aqueous solution at 18° changes gradually from  $[\alpha]_D - 20.75^\circ$  to about +10; when boiled with *N*/10 sulphuric acid, they lose all their nitrogen as ammonia, and the solution has then a rotatory power about equal to that of *d*-glucose. C. F. B.

**An Ammoniacal Derivative of Fructose.** By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1899, 18, 72—76).—When fructose (*lævulose*) is dissolved in methyl-alcoholic ammonia, and the solution is allowed to remain for several months so that air has limited access to it, the optical activity gradually disappears, and a deposit forms which can be recrystallised from hot water. This substance has no definite melting point, but blackens at 210—220°; it has the composition C<sub>6</sub>H<sub>9</sub>NO<sub>4</sub>, and the specific rotation is  $[\alpha]_D - 75^\circ$  in 0.4 and  $-80^\circ$  per cent. in 1 per cent. aqueous solution. It reduces Fehling's solution on warming, and is reduced by sodium amalgam, but it does not form an

osazone or react with nitrous acid, or yield ammonia when boiled with acids, and it is without basic properties. It forms a *tetracetyl* derivative which melts at  $174^{\circ}$ , and has a specific rotation  $[\alpha]_D - 6.7^{\circ}$  in 2.4 per cent. chloroform solution. C. F. B.

**Formation of Pentabromacetone from Acetonedicarboxylic Acid.** By B. BERGESIO and LUIGI SABBATANI (*Chem. Centr.*, 1899, i, 596; from *Ann. Farm. Chim.*, 1898, 529—532).—By the action of bromine on dry acetonedicarboxylic acid or on its aqueous solution, pentabromacetone is formed; it melts at  $74^{\circ}$ , and when treated with silver nitrate loses 3Br. In Stahre's method of distinguishing citric from tartaric acid, acetonedicarboxylic acid and pentabromacetone are formed as intermediate products. E. W. W.

**Action of Reducing Agents on Nitro-Compounds of the Methane Series and their Derivatives. I. A Method of Converting Primary and Secondary Nitro-compounds into the corresponding Oximes, Ketones, and Aldehydes.** By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 597—598; from *J. Russ. Chem. Soc.*, 1898, 30, 960—964).—The ketone is prepared from the potassium salt of the nitro-compound by adding an aqueous solution of the latter drop by drop to a solution of stannous chloride in concentrated hydrochloric acid containing 30—50 per cent. more than the theoretical quantity of chloride. The liquid is well shaken, the product distilled in steam, and the ketone separated from the distillate by means of potassium carbonate. Nitrohexamethylene, when treated in this way, yields 80 per cent. of hexamethylene ketone, and by treating the product with sodium carbonate before distilling in steam the oxime is obtained; it melts at  $89.5$ — $90.5^{\circ}$  and boils at  $206$ — $210^{\circ}$ . Nitro-octane and nitro-di-isoamyl were treated by this method and phenyl-nitromethane yields the corresponding aldehyde and oxime. By the action of concentrated hydrochloric acid on salts of nitro-compounds, isonitro-compounds are formed and the latter, when reduced with stannous chloride, yield the oximes. The ketones or aldehydes are prepared by boiling the oximes with acids. E. W. W.

**Action of Alkalis on Chloro-ketones and Chlor-alcohols.**—By J. SALKIND (*Chem. Centr.*, 1899, i, 596—597; from *J. Russ. Chem. Soc.*, 1898, 30, 906—914).—Trichlorethylideneacetone (anhydrochloralacetone) is prepared by allowing a solution of chloralacetone in concentrated sulphuric acid to remain 12 hours and then pouring the mixture on to ice; this method gives a 75—80 per cent. yield. Trichlorethylideneacetone forms colourless crystals, melts at  $25$ — $26^{\circ}$ , boils at  $93$ — $94^{\circ}$  under 20 mm. pressure, is easily soluble in alcohol, ether, benzene, light petroleum, chloroform, or acetone, and insoluble in water. By the action of hydroxylamine (1 mol.) on trichlorethylideneacetone, a small quantity of the compound,  $C_5H_7Cl_2NO_2$ , is formed; it crystallises from benzene in prisms, melts and decomposes at  $124$ — $126^{\circ}$ , is soluble in alcohol, ether, acetone, hot chloroform, hot light petroleum, or hot benzene, rather sparingly soluble in hot water, and insoluble in carbon bisulphide. By the further action of hydroxylamine on this compound, or by the action

of hydroxylamine (2 mols.) on trichlorethylideneacetone, the compound,  $C_5H_8Cl_2N_2O_2$ , is obtained; it crystallises from a mixture of benzene and alcohol, melts and decomposes at  $155^\circ$ , is easily soluble in alcohol, ether, or acetone, soluble in hot benzene or hot water, rather sparingly soluble in hot chloroform, and insoluble in light petroleum. By the action of a 10 per cent. solution of potassium hydroxide on chloralacetone or on trichlorethylideneacetone, Uschakoff's acid,  $C_5H_5ClO_2$  (*J. Russ. Chem. Soc.*, 1897, 29, 113), is formed. The yield in the former case is 1, in the latter 7 per cent., and 6 per cent. of this compound is also obtained by treating trichlorethylideneacetone with alcoholic potash. A 10 per cent. solution of sodium ethoxide decomposes chloralacetone, but by the action of a 4 per cent. solution, a small quantity of this acid is formed together with an acid syrup.

E. W. W.

**Mixed Anhydrides of Formic Acid.** By AUGUSTE BÉHAL (*Compt. rend.*, 1899, 128, 1460—1463).—On mixing formic acid and acetic anhydride, in molecular proportions, a certain amount of *formic acetic anhydride* is produced. Its amount may be estimated by acting on the liquid in the cold with a tertiary base such as quinoline, pyridine, or dimethylaniline, which decomposes it with the evolution of carbonic oxide,  $COMe \cdot O \cdot COH = CO + MeCOOH$ ; the volume of the liberated gas gives the quantity of mixed anhydride. The mixture of formic acid and acetic anhydride is distilled, the first portions of the distillate containing the formic acid being rejected; the formic acetic anhydride can then be separated partly by fractional distillation and partly by its slight solubility in light petroleum.

Formic acetic anhydride is a mobile liquid with a strong tear-producing odour; it boils at  $29^\circ$  under 17 mm. pressure, and at ordinary pressures distils and decomposes at  $105$ — $120^\circ$ . It acts on alcohols, giving the corresponding formates and acetic acid, but no trace of the acetates. With ammonia, aniline, methylaniline, para-ethoxyaniline and orthamidophenol, it gives the corresponding formamides, and with urea and phenylhydrazine it yields monoformyl derivatives.

T. H. P.

**Oxidation of Halogen-substitution Derivatives of Ethylene.** By FRÉDÉRIC SWARTS (*Chem. Centr.*, 1899, i, 588—589; from *Bull. Acad. roy. Belg.*, 1898, [iii], 36, 532—552).—By the action of oxygen on difluorodibromethylene, fluorodibromacetic acid is the only product, and difluorobromacetic acid is not formed (compare Abstr., 1898, i, 457). Fluorotribromethylene, when oxidised by oxygen at  $100^\circ$ , yields fluoropentabromethane and a liquid boiling at  $130$ — $160^\circ$ , which contains ethylic fluorodibromacetate and tribromacetate. By the oxidation of fluorodibromethylene,  $CBr_2 \cdot CHF$ , *fluorobromacetic bromide*, which boils at  $116^\circ$ , is obtained, together with a small quantity of ethylic dibromacetate and hydrogen fluoride; the two latter are probably formed from dibromacetic fluoride. *Ethylic fluorobromacetate*,  $CHBrF \cdot COOEt$ , boils at  $150^\circ$ . When perchlorethylene is oxidised with ozone, trichloracetic chloride is formed; it cannot, however, be separated from perchlorethylene by distillation, but the trichloracetamide, prepared by treating the product with ammonia, separates from



boiling chloroform in colourless crystals and melts at  $141^{\circ}$ . Tribromacetamide, prepared from tetrabromomethylene in a similar manner, melts at  $120^{\circ}$ , and dichlorodibromomethylene yields a compound which melts at  $127^{\circ}$ , and is probably chlorodibromacetamide. Per-substituted ethylenes are more or less easily oxidised by oxygen, the most active halogen remaining combined with the CO group. Symmetrical dibromethylene is only very slowly attacked by ozone, yielding a product of complex composition, from which unsymmetrical tetrabromomethane,  $\text{CBr}_3 \cdot \text{CH}_2\text{Br}$ , boiling at  $235^{\circ}$ , dibromaldehyde boiling at  $145^{\circ}$ , a small quantity of bromacetic bromide, and an acid were isolated; the last compound boils at  $225^{\circ}$ , and is probably dibromacetic acid. To account for the oxidation of these compounds, the author inclines to Henry's theory that an unstable ethylenic oxide is formed by direct combination with oxygen.

E. W. W.

**Di-isoamylacetic Acid.** By H. FOURNIER (*Compt. rend.*, 1899, 128, 1288—1289).—*Di-isoamylacetic acid*,  $\text{CH}(\text{C}_5\text{H}_{11})_2 \cdot \text{COOH}$ , is obtained by heating di-isoamylmalonic acid at a temperature of about  $175^{\circ}$ . When crystallised from dilute alcohol or from benzene, it forms white needles which melt at  $46$ — $47^{\circ}$ , and are insoluble in water, but dissolve readily in organic solvents. *Di-isoamylacetamide*, prepared from the acid chloride, forms silky, white needles which melt at  $115^{\circ}$ .

Di-isoamylmalonic acid is obtained from its ethylic salt, which is prepared by the action of isoamyllic bromide and sodium ethoxide on ethylic isoamylmalonate. It forms white lamellæ which melt at  $147$ — $148^{\circ}$ , and are very soluble in ether, alcohol, or benzene, but only slightly in carbon bisulphide, and not at all in water.

C. H. B.

**Alternation in Volatility in the Series of the Chlorides of the Normal Acids.** By LOUIS HENRY (*Rec. Trav. Chim.*, 1899, 18, 247—254).—In the series of the chlorides of the normal acids, the boiling point rises by a greater amount in passing from a compound with an even number of carbon atoms to the next homologue with an odd number than in the opposite case, as the following table shows; the difference between successive odd members is approxi-

Diff. between even members.	No. of C atoms.	Formula.	Boiling point.	Successive differences.	Diff. between odd members.
48—50°	$\text{C}_2$	$\text{CH}_3 \cdot \text{COCl}$	51—52°	26—29°	47—50°
	$\text{C}_3$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COCl}$	78—80		
	$\text{C}_4$	$\text{CH}_3 \cdot [\text{CH}_2]_2 \cdot \text{COCl}$	100—101		
44—46	$\text{C}_5$	$\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{COCl}$	127—128	17—19	46—48
	$\text{C}_6$	$\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{COCl}$	145—146		
48—50	$\text{C}_7$	$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{COCl}$	174—175	19—21	45—46
	$\text{C}_8$	$\text{CH}_3 \cdot [\text{CH}_2]_6 \cdot \text{COCl}$	194—195		
	$\text{C}_9$	$\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{COCl}$	220		
49—50	$\text{C}_4$	$\text{CHMe}_3 \cdot \text{COCl}$	92	21—22	—
	$\text{C}_5$	$\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{COCl}$	113—114		
	$\text{C}_6$	$\text{CHMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{COCl}$	141—142		

mately equal, as is that between successive even members, and, moreover, the two differences are equal.

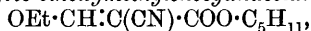
The corresponding alcoholic chlorides ( $R \cdot CH_2Cl$  instead of  $R \cdot COCl$ ) exhibit no such alternation. Three acid chlorides containing an isopropyl group exhibit a similar alternation, however, except that here the greater increase is from odd to even, as seen in the lower section of the table.

Similar alternations have long been observed in the case of melting points; this appears to be the first instance in the case of boiling points. C. F. B.

**Vinylacetic Acid.** By JOHANNES WISLICENUS (*Ber.*, 1899, 32, 2047—2048).— $\beta$ -Bromoglutaric acid (Ssemenoff, *J. Russ. Chem. Soc.*, 1899, 31, 115), obtained when the  $\beta$ -hydroxy-acid is heated with saturated hydrobromic acid at  $100^\circ$  in sealed tubes, forms crystalline plates melting at  $137^\circ$ . When neutralised with aqueous sodium hydroxide and the solution warmed, carbonic anhydride is evolved and the solution becomes acid. When dilute sulphuric acid is added, the mixture submitted to distillation in steam, and the distillate extracted in a Hagemann's apparatus, a syrupy acid is obtained. The calcium salt of this acid crystallises in colourless plates having the composition  $(C_4H_5O_2)_2Ca + H_2O$ . From its method of preparation, it is concluded that the acid must be vinylacetic acid, and it follows that the acid obtained from ethylenemalononic acid and described by Fittig and Roeder (*Abstr.*, 1885, 653) as vinylacetic acid, but by Perkin (*Trans.*, 1885, 815) as trimethylenecarboxylic acid, cannot be vinylacetic acid, since its calcium salt crystallises with  $6H_2O$ . J. J. S.

**Oxymethylene Derivatives of Alkyl Cyanacetates.** By E. GRÉGOIRE DE BOLLEMONT (*Compt. rend.*, 1899, 128, 1338—1341).—When amylic formate acts on dry ethylic sodiocyanacetate at  $100^\circ$ , it yields sodium ethylic formylcyanacetate, and if this is treated with barium chloride, the salt  $Ba[O \cdot CH : C(CN) \cdot COO \cdot C_5H_{11}]_2$  is obtained in nacreous leaflets very soluble in alcohol, but only very slightly so in ether. The corresponding silver salt is a crystalline, white powder slightly soluble in hot water, from which it crystallises in groups of small needles.

When amylic cyanacetate and ethylic orthoformate are treated with acetic anhydride, amylic ethoxymethylenecyanacetate,



is obtained; it boils at about  $211^\circ$  under 35 mm. pressure. The ethylic compound forms white needles which melt at about  $52^\circ$  and dissolve readily in alcohol and in ether; the methylic compound forms elongated tablets which melt at about  $34^\circ$  and are very soluble in alcohol. The barium salt, obtained by the action of barium hydroxide on the amylic, ethylic, or methylic compound, is identical with that obtained from the product of the action of amylic formate on ethylic sodiocyanacetate.

Methylic orthoformate behaves in the same way as the ethylic compound in these reactions. Methylic methoxymethylenecyanacetate,

OMe·CH:C(CN)·COOMe, forms slender, transparent needles which melt at about 88°, whilst *ethylic methoxymethylenecyanacetate* forms transparent rhombs which melt at about 99°. C. H. B.

**Reaction between Aliphatic Thiocyanates and Metallic Derivatives of Ethylic Acetoacetate and Analogous Substances.** By ELMER P. KOHLER (*Amer. Chem. J.*, 1899, 22, 67—80). —When ethylic cupracetoacetate dissolved in absolute alcohol is heated with ethylic thiocyanate (1 mol.), copper mercaptide is precipitated, and a mixture of ethylic bisulphide, ethylic acetoacetate, and *ethylic cyanocupracetoacetate*,  $(C_7H_5O_3N_2)_2Cu$ , obtained; the last crystallises from alcohol, in which it is sparingly soluble, in small, dark green plates, and, unlike ethylic cupracetoacetate, is not decomposed by boiling with water or alcohol, although, when warmed with dilute sulphuric acid, it readily yields ethylic cyanacetate. It appears probable that in this reaction ethylic cyanacetate and the copper derivative,  $(Et_2S)_2Cu$ , of ethylic disulphide are initially formed, and that the ethylic cyanacetate then interacts with ethylic cupracetoacetate, forming ethylic acetoacetate and cupricyanacetate; the ethylic bisulphide is formed by its copper derivative undergoing decomposition to form copper mercaptide. Methylic, propylic, isopropylic, and benzylic thiocyanates interact with ethylic cupracetoacetate in the same manner as ethylic thiocyanate.

Ethylene dithiocyanate interacts with cold alcoholic ethylic cupracetoacetate to form *copper thiocyanomercaptide*,  $CNS \cdot CH_2 \cdot CH_2 \cdot SCu$ , and *symmetrical dithiocyanethylic bisulphide*,  $(CNS \cdot CH_2 \cdot CH_2 \cdot S)_2$ ; the former is a white, insoluble solid which slowly dissolves in boiling concentrated hydrochloric acid, yielding *iminotrimethylenebisulphide hydrochloride*,  $\begin{matrix} CH_2 \cdot S \\ CH_2 \cdot S \end{matrix} > C:NH, HCl$ , and is oxidised by fuming nitric acid to 1:2-ethanedisulphonic acid. Symmetrical dithiocyanethylic bisulphide, best prepared by shaking copper thiocyanomercaptide with water and iodine, is a colourless liquid which does not solidify at  $-20^\circ$ , and, when warmed with concentrated caustic potash, gives rise to ethylene tetrasulphide; it does not interact with ethylic cupracetoacetate in the cold, but at the temperature of boiling alcohol yields ethylic cupricyanacetate, and a mixture of several sulphur compounds. This explains the complexity of the product obtained on heating ethylenic dithiocyanate with alcoholic ethylic cupracetoacetate. When ethylenic dithiocyanate (1 mol.) is gradually added to a boiling solution of ethylic cupracetoacetate in absolute alcohol, both of the thiocyano-groups enter into action, and ethylenic tetrasulphide is formed together with ethylic cupricyanacetate, ethylic acetoacetate, and the copper derivative,  $C_2H_4S_2Cu_2$ , of ethylene mercaptan.

$\alpha\beta$ - and  $\alpha\gamma$ -Dithiocyanopropane interact with ethylic cupracetoacetate in the same manner as ethylene dithiocyanate. Methylenethiocyanate yields a dark brown, insoluble *product*,  $CH_2S_2Cu_2$ , probably *copper methylene mercaptide*, but possibly a mixture of cuprous sulphide and the *mercaptide*,  $(SCu \cdot CH_2 \cdot S)_2$ ; the latter assumption would account for its evolving hydrogen sulphide and giving rise to a

light yellow powder,  $C_2H_4S_3Cu_2$ , when left in contact with concentrated hydrochloric acid.

Ethylic thiocyanate does not interact as definitely with ethylic sodacetoacetate as with ethylic cupracetoacetate; this is due to the soluble mercaptide produced decomposing the ethylic acetoacetate and cyanacetoacetate initially formed. The best results are obtained by leaving dry ethylic sodacetoacetate in contact with an excess of ethylic thiocyanate in cold absolute ether, when 60 per cent. of the theoretical yield of ethylic cyanacetoacetate is obtained. From ethylic sodethylacetoacetate, under similar conditions, *ethylic cyanethylacetoacetate*,  $C_9H_{13}O_3N$ , was obtained as an oil boiling at  $130^\circ$  under 35 mm. pressure.

Whereas ethylic cupracetoacetate interacts with chlorethylic thiocyanate in the same manner as with ethylic thiocyanate, the chlorine atom present being without influence, ethylic sodacetoacetate gives rise principally to *ethylic thiocyanethylacetoacetate*,  $CNS \cdot CH_2 \cdot CH_2 \cdot CHAc \cdot COOEt$ , which crystallises from light petroleum in colourless plates or needles and melts at  $83^\circ$ ; a considerable proportion of ethylic cyanosodacetoacetate is, however, also formed.

W. A. D.

**Relations between the Melting Points and Molecular Weights of the Normal and Non-normal Acids of the Oxalic Acid Series.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1899, [iii], 21, 578—580, and 580—583).—From the melting points collected in the following table:

$C_2$ Oxalic acid .....	$212^\circ$	$C_3$ Malonic acid.....	$132^\circ$
$C_4$ Succinic acid .....	180	$C_5$ Glutaric acid .....	97
$C_6$ Adipic acid.....	148	$C_7$ Normal pimelic acid..	103
$C_8$ Suberic acid .....	140	$C_9$ Normal azelaic acid...	117.5
$C_{10}$ Sebacic acid.....	127		

it is seen that for the normal acids of the oxalic acid series, (1) each term of the even series melts at a higher temperature than either of its two contiguous homologues of the odd series, and (2) the odd series shows a minimum melting point for the  $C_5$  acid, as is the case for the normal fatty acids.

Among the non-normal acids of this series, very few comparable data are known. The most complete series is that of the malonic acids mono-substituted with a normal lateral chain:

	Even.	Odd.
$C_4$ Methylmalonic acid .....	$130^\circ$	—
$C_5$ Ethylmalonic acid.....	—	$111.5^\circ$
$C_6$ Normal propylmalonic acid .....	$93.5$	—
$C_7$ Normal butylmalonic acid .....	—	$98.5$
$C_8$ Normal pentylmalonic acid.....	82	—
$C_{10}$ Normal heptylmalonic acid .....	$97.5$	—

This series shows a minimum melting point, which is also that of the acid with  $C_5$  in the lateral chain, and further, it is seen that an acid of the even series melts at a lower temperature than either of its two contiguous homologues in the odd series. Other series are given,

but are very incomplete, and in all of them the melting point falls as the molecular weight increases. T. H. P.

**Stability of Solutions of Oxalic Acid.** By W. P. JORISSEN (*Zeit. angew. Chem.*, 1899, 521—525).—A sterilised normal solution of oxalic acid suffered no decomposition in the dark, even after 101 days, but when exposed to the light it lost, in 57 days, so much acid that its strength was reduced from  $N\ 0.99$  to  $N\ 0.965$ ; after 101 days exposure, this was reduced to  $N\ 0.926$ . A solution containing 10 grams of oxalic acid and 50 c.c. of sulphuric acid per litre also kept well in the dark, but exposure to light for 37 days reduced its strength from 0.1592 to 0.1420. A solution containing 10 grams of oxalic and 1 gram of boric acid per litre did not suffer any diminution of strength in the dark, but in the light its strength was reduced from 0.1592 to 0.1523 in 37 days. A centinormal solution of oxalic acid containing also 1 gram of boric acid per litre did not lose in strength in the dark, but when exposed to the light its acidity was reduced from 0.01002 to 0.002, and after 78 days to *nil*.

A centinormal solution of oxalic acid mixed with mould (which had been cultivated on moist bread) was reduced in strength from 0.00992 to 0.00927 when kept in the dark for 62 days; in a second experiment, the acid completely disappeared when kept in the dark for 56 days. The mould has, however, no appreciable action on decinormal or centinormal solutions when these contain in addition 50 c.c. of sulphuric acid per litre. A centinormal solution containing 1 gram of boric acid per litre and mixed with the mould was reduced in strength from 0.01002 to 0.00711 when kept in the dark, in winter time, for 62 days; from 0.0100 to 0.00926 at the summer temperature in 56 days. When 2 grams of boric acid were used, there was no loss when kept for 62 days in winter time, but 44 days exposure in summer time reduced the strength from 0.01010 to 0.00916. Addition of alcohol was also tried, a decinormal solution of oxalic acid in water containing 12.4 per cent. of alcohol being exposed for 36 days in the dark, when the strength had diminished from 0.0984 to 0.0931; when exposed to the light, it diminished from 0.0984 to 0.0716; addition of twice the amount of alcohol gave no better results. The action in the dark is probably due to the formation of ethylic oxalate.

Further experiments are appended showing that sulphuric and boric acids increase the velocity of oxidation of oxalic acid in the light. A remarkable action is exercised by manganous sulphate, for this salt, whilst acting as a preservative in the light, actually promotes the oxidation of the acid in the dark. L. DE K.

**Action of Acidic Metallic Oxides on Organic Acid.** By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1899, 21, 1—18).—*Decomposition of aluminium, chromium, and iron oxalates with metallic chlorides* [with MAX PLATSCH].—A concentrated solution of ammonium aluminium oxalate,  $\text{Al}(\text{CO}_2 \cdot \text{COO} \cdot \text{NH}_4)_3 + 2\frac{1}{2}\text{H}_2\text{O}$ , when treated with the equivalent quantity of barium chloride, yields a large quantity of barium oxalate if the barium chloride is added all at once. If, however, the barium chloride is added gradually, only a very small precipitate is obtained, and the filtrate after a time deposits the double salt,

$\text{Al}(\text{C}_2\text{O}_4)_3\text{BaNH}_4 + 2\text{H}_2\text{O}$ , in silky, white needles. This salt is much more unstable than the alkali aluminium oxalates, and decomposes when treated with warm water into barium oxalate and aluminium oxalate, whereas the alkali aluminium oxalates crystallise from boiling water without decomposition. With strontium chloride, the ammonium aluminium oxalate yields a small quantity of strontium oxalate, and the *salt*,  $\text{Al}(\text{C}_2\text{O}_4)_3\text{SrNH}_4 + 5\text{H}_2\text{O}$ , which is not so stable as the preceding barium salt. With calcium, magnesium, and zinc chlorides, the ammonium aluminium oxalate is completely decomposed. With cobalt chloride, cobalt oxalate is first precipitated, then the double salt,  $\text{NH}_4\text{CoCl}_3 + 6\text{H}_2\text{O}$ , and finally the salt  $(\text{NH}_4)_2\text{O}, \text{Al}_2\text{O}_3, 4\text{C}_2\text{O}_3$ , mixed with a small quantity of ammonium chloride. A similar reaction takes place with nickel, cadmium, or copper chloride.

The blue ammonium chromoxalate,  $\text{Cr}(\text{CO}_2 \cdot \text{COO} \cdot \text{NH}_4)_3, 3\text{H}_2\text{O}$ , when treated with barium chloride, yields a small quantity of barium oxalate, and the *salt*  $[\text{Cr}(\text{C}_2\text{O}_4)_3]_2\text{Ba}_3 + 14\text{H}_2\text{O}$ , which crystallises in bluish-green needles, and is decomposed by warm water. With strontium chloride, it yields a large quantity of strontium oxalate, and the *salt*  $\text{Cr}(\text{C}_2\text{O}_4)_3\text{SrNH}_4 + 5\text{H}_2\text{O}$ , which crystallises in bluish-green needles, and is very unstable. With calcium, magnesium, or zinc chloride at ordinary temperatures, decomposition takes place with the formation of metallic oxalates, ammonium chloride, and acid chromium oxalate; but with calcium chloride at  $-15^\circ$ , the *double salt*,  $\text{Cr}(\text{C}_2\text{O}_4)_3\text{CaNH}_4$ , is obtained, which crystallises in needles, and at the ordinary temperature at once decomposes, yielding calcium oxalate. With cobalt, nickel, or copper chloride, a reaction takes place similar to that obtained with ammonium aluminium oxalate and the metallic oxalates; metallic ammonium chlorides and the red ammonium chromoxalate are produced. With cadmium chloride, cadmium oxalate and cadmium ammonium chloride crystallise out first, and the mother liquors yield the *salt*  $\text{Cr}(\text{C}_2\text{O}_4)_3\text{CdNH}_4 + 10\text{H}_2\text{O}$ , which crystallises in dark blue prisms.

The red potassium chromoxalate,  $\text{C}_2\text{O}_4\text{Cr} \cdot \text{C}_2\text{O}_4\text{K} + 5\text{H}_2\text{O}$ , when treated with barium chloride, yields the *double salt*  $\text{Cr}(\text{C}_2\text{O}_4)_3\text{BaK} + 2\text{H}_2\text{O}$ , which crystallises in bluish-green needles. The mother liquors yield a non-crystallisable syrup free from oxalic acid. With strontium chloride, a similar reaction takes place, and the *salt*  $\text{Cr}(\text{C}_2\text{O}_4)_3\text{SrK} + 4\text{H}_2\text{O}$  is obtained. With calcium, magnesium, copper, or cadmium chlorides no reaction takes place.

Ammonium ferrioxalate,  $\text{Fe}(\text{C}_2\text{O}_4 \cdot \text{NH}_4)_3, 3\text{H}_2\text{O}$ , yields, with barium chloride, a considerable quantity of barium oxalate, and the *salt*  $[\text{Fe}(\text{C}_2\text{O}_4)_3]_2\text{Ba}_3 + 22\text{H}_2\text{O}$ . With strontium chloride, it yields a larger quantity of strontium oxalate, and the *salt*  $\text{Fe}(\text{C}_2\text{O}_4)_3\text{SrNH}_4 + 6\text{H}_2\text{O}$ . With calcium chloride and other metallic chlorides, complete decomposition takes place.

*Salts of Molybdanumoxalic and Vanadiumoxalic Acids* [with HERMANN ITZIG.]—*Sodium molybdanumoxalate*,  $\begin{matrix} \text{CO} \cdot \text{O} \\ | \quad \diagup \\ \text{CO} \cdot \text{O} \end{matrix} \text{MoO}(\text{ONa})_2 + 3\text{H}_2\text{O}$ , is obtained by adding the theoretical quantity of molybdic acid to a boiling solution of sodium oxalate, and after concentrating to a syrup on the water-bath, allowing the mixture to crystallise over sulphuric

acid; it crystallises in white, interlacing needles, and is very soluble. The salt  $C_2O_4(MoO_2 \cdot ONa)_2 + 6H_2O$ , obtained by saturating a boiling solution of sodium oxalate with molybdic acid, separates in white, microscopic crystals. The corresponding *barium* salt with  $3\frac{1}{2}H_2O$ , obtained by shaking barium oxalate suspended in water with the theoretical quantity of molybdic acid at the ordinary temperature for 3—4 hours, crystallises in white needles and dissolves in water at  $50^\circ$ , but on keeping the solution, decomposition occurs with the formation of barium molybdate and barium oxalate.

*Barium vanadium oxalate*,  $Ba_3V_2O_5(C_2O_4)_4 + 15H_2O$ , is obtained by treating ammonium vanadium oxalate with barium chloride, crystallises in small, yellow needles, and is sparingly soluble in water.

[With IVAN KOPPEL.]—A table of the electric conductivity of the salts of the complex oxalic acids is given. E. C. R.

**Potassium Plato-oxalonitrite.** By MAURICE VÈZES (*Bull. Soc. Chim.*, 1899, [iii], 21, 481—487).—This double salt has been already fully described (*Abstr.*, 1898, i, 64). It forms monoclinic prisms [ $a:b:c = 0.4131:1:0.3340$ ;  $\beta = 111^\circ 39' 51''$ ]. R. H. P.

**A Lower Homologue of Citric Acid.** By AUGUSTIN DURAND (*Compt. rend.*, 1899, 128, 1525—1527).—By a method similar to that employed by Haller and Held for preparing citric acid synthetically (*Abstr.*, 1891, 178), the author has obtained the next lower homologue, namely,  $COOH \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH$ . A mixture of an ethereal solution of ethylic oxalacetate with potassium cyanide and hydrochloric acid gives the cyanhydrin  $COOEt \cdot C(OH)(CN) \cdot CH_2 \cdot COOEt$ , which, on hydrolysis, yields  $COOEt \cdot C(OH)(COOH) \cdot CH_2 \cdot COOEt$ . The *acid*, obtained by decomposing the lead salt with hydrogen sulphide, forms a light yellow syrup with a taste resembling that of citric acid. On neutralising the acid with lime water, the *calcium* salt is slowly deposited in mammillary tufts of shining, white crystals containing  $5\frac{1}{2}H_2O$ . The *zinc* salt is precipitated as a white powder. T. H. P.

**Preparation of Mucobromic and Mucochloric Acids.** By HUGO SIMONIS (*Ber.*, 1899, 32, 2084—2086. Compare Schmelz and Beilstein, *Annalen, Supp.*, 3, 276; Jackson and Hill, *Abstr.*, 1878, 402; 1879, 224).—Mucobromic acid is best obtained in large quantities by the following process:—Furfuraldehyde is covered with about 10 times its weight of water and is then treated with 10 times its weight of bromine, which is run in fairly quickly; the reaction is violent and is completed by boiling the mixture for at least about 15 minutes. When the solution is evaporated to a small bulk, the acid separates out and may be recrystallised from hot water. The yield is nearly theoretical. Mucochloric acid may be obtained in a similar manner by using furfuraldehyde, manganese dioxide, and hydrochloric acid. J. J. S.

**Derivatives of Cyclopentane and of Dipentamethenyl.** By WILHELM MEISER (*Ber.*, 1899, 32, 2049—2057).—Wislicenus's cyclopentanol (*Abstr.*, 1893, i, 556) reacts with an alcoholic solution of phenylcarbimide, yielding the *phenylurethane*,  $C_5H_9 \cdot O \cdot CO \cdot NHPh$ , which

crystallises from alcohol in colourless needles melting at  $132.5^{\circ}$ . A good yield of cyclopentene (*loc. cit.*) may be obtained by the action of alcoholic potash on bromocyclopentane, a small amount of *penta-methenylic ethylic ether*,  $C_5H_9 \cdot OEt$ , being also formed; the latter is a colourless liquid boiling at  $126-127^{\circ}$ . *Cyclopentenediol*,  $C_5H_8(OH)_2$ , obtained when cyclopentene dibromide is boiled with potassium carbonate solution, is an extremely hygroscopic, crystalline solid distilling at  $226.5-227^{\circ}$  under ordinary atmospheric pressure, or at  $126.5-127.5^{\circ}$  under 12 mm. pressure; when freshly distilled, it melts at  $48-49.5^{\circ}$ , is readily soluble in alcohol or water, and has a sweet odour. The *diacetate*,  $C_5H_8(OAc)_2$ , is a thick liquid boiling at  $224-226^{\circ}$ ; the *diphenylurethane*,  $C_5H_8(O \cdot CO \cdot NHPh)_2$ , crystallises from benzene in minute, colourless needles melting at  $211-212^{\circ}$  and is sparingly soluble in the usual solvents. *2-Chlorocyclopentanol*,  $C_5H_8Cl \cdot OH$ , obtained by leading dry hydrogen chloride into the glycol heated at  $170-190^{\circ}$ , is a colourless oil distilling at  $78^{\circ}$  under 13 mm. pressure and volatile in steam; it is also formed by the addition of hypochlorous acid to cyclopentene, and yields a *phenylurethane*,  $C_5H_8Cl \cdot O \cdot CO \cdot NHPh$ , crystallising in colourless needles and melting at  $107-108^{\circ}$ . When the chlorhydrin is heated with concentrated aqueous potassium hydroxide, water and *cyclopentenic oxide*,  $C_5H_8O$ , distil over. This is a colourless oil with an unpleasant odour; it distils at  $102^{\circ}$ , and in many properties resembles ethylenic oxide, but its oxygenated ring is even more readily broken than that of ethylenic oxide; for example, the oxide combines with hydrogen chloride instantaneously at  $-18^{\circ}$ , yielding the original chlorocyclopentanol.

*Dipentamethenylpinacone*,  $C_4H_8 \cdot C(OH) \cdot C(OH) \cdot C_4H_8$ , may be isolated from the reduction products of cycloketopentane, if the alcohol,  $C_5H_9 \cdot OH$ , is first distilled off under atmospheric pressure, the residue then submitted to distillation under reduced pressure, and the fraction passing over at  $130-160^{\circ}$  under 17 mm. pressure collected separately. After crystallisation from a mixture of benzene and light petroleum, it forms colourless, glistening pyramids melting at  $106.5-108^{\circ}$ . The residue left after the pinacone has been distilled consists of the *anhydride*,  $C_{20}H_{32}O_2$ , of the pinacone and crystallises in glistening needles melting at  $161.3-162.3^{\circ}$ . When the pinacone is warmed with dilute sulphuric acid, it loses water and becomes transformed into the *pinacolin*,  $\begin{array}{c} CH_2 \cdot CH_2 \\ | \quad \quad | \\ CH_2 \cdot CH_2 \end{array} > C < \begin{array}{c} CH_2 \cdot CH_2 \\ | \quad \quad | \\ CO \cdot CH_2 \end{array} > CH_2$ ; this is a pale yellow, somewhat thick oil distilling at  $105-108^{\circ}$  under 19.5 mm. pressure; it has a strong odour of peppermint, is volatile with steam and readily reacts with bromine or potassium permanganate. The *oxime*,  $C_{10}H_{16} \cdot N \cdot OH$ , crystallises in plates and prisms melting between  $55^{\circ}$  and  $60^{\circ}$ , and according to the author is probably a mixture of stereoisomeric forms. When oxidised with nitric acid, the pinacolin yields carbonic anhydride and succinic acid, but the chief product is a syrupy dibasic *acid*,  $C_{10}H_{16}O_4$ , the silver salt of which,  $C_{10}H_{14}O_4Ag_2$ , has been prepared and analysed. The conversion of the pinacone into the pinacolin is interesting as it is one of the first cases observed of the conversion of a pentacyclic into a hexacyclic carbon compound.

*Dipentamethenyl*,  $C_5H_9 \cdot C_5H_9$ , obtained by the action of sodium on



an ethereal solution of bromocyclopentane, is a colourless oil boiling at 189—191°. J. J. S.

**Cyclic Isomeric Change of Acetylmethylheptenone.** By GEORGES LESER (*Bull. Soc. Chim.*, 1899, [iii], 21, 546—549. Compare Abstr., 1898, i, 512, and this vol., i, 479).—When acetylmethylheptenone is allowed to remain for two hours with six times its weight of 80 per cent. sulphuric acid, and is then diluted with water and extracted with ether, the isomeric 2-acetyl-1:1-dimethylcyclohexanone-3,  $\text{CMe}_2 \begin{smallmatrix} \text{CHAc} \cdot \text{CO} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} \text{CH}_2$ , is obtained as an oil having a penetrating smell and boiling at 110—111° under 12 mm. pressure. Its alcoholic solution gives a violet-red coloration with ferric chloride, and it forms a *semicarbazone* melting at 168°. With aqueous potash, it yields 1:1-dimethylcyclohexanone-3, which boils at 173—174°, and yields a *semicarbazone* melting at 198°. 2-Acetyl-1:1-dimethylcyclohexanone-3, on treatment with alcoholic potash, yields a *ketonic acid*,  $\text{COMe} \cdot \text{CH}_2 \cdot \text{CMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{COOH}$ , which boils at 190—191° under 20 mm. pressure, yields an *oxime* melting at 101—101·5° (not at 98° as previously described, *loc. cit.*) and a *semicarbazone* melting at 161°. On treatment with bromine and caustic soda, it is oxidised to normal  $\beta$ -dimethylpimelic acid, which forms long prisms melting at 104° (101—102·5°, according to von Baeyer), and on distillation with soda-lime, is reconverted into 1:1-dimethylhexanone-3. R. H. P.

**Action of Ferric Chloride and Bromide on Aromatic Hydrocarbons and their Haloid Substitution Derivatives.** By VICTOR THOMAS (*Compt. rend.*, 1899, 128, 1576—1578. Compare Abstr., 1898, i, 640, and this vol., i, 26).—In addition to the products of the action of ferric chloride on paradibromobenzene already mentioned (*loc. cit.*), the author has now separated parabromochlorobenzene, already prepared by Griess and Körner, and two trichlorobromobenzenes melting at 93° and 138° respectively, and crystallising in slender needles, which readily sublime and are soluble in the ordinary organic solvents.

Iodo-derivatives of aromatic hydrocarbons are readily chlorinated by ferric chloride, iodobenzene, for example, giving parachloriodobenzene, hydrogen chloride being evolved in large quantities; with di-iodobenzene, the action is even more energetic, iodine being freely liberated, and chloriodo-derivatives containing only 1 atom of iodine in the molecule being formed.

In general, ferric bromide acts on aromatic hydrocarbons in a similar manner to, but less energetically than, the chloride. With benzene, the action is very slow at ordinary temperatures, but becomes very rapid on boiling for some hours, the mass carbonising and bromobenzenes being formed. In the case of toluene, the action begins at about 60°, and continues steadily on boiling, less charring and better yields of the bromo-derivatives being obtained than with benzene.

Chlorinated benzenes are rapidly attacked by ferric bromide, chlorobenzene giving the parachlorobromo-compound. With more highly

chlorinated benzenes, the whole series of chlorobromo-derivatives can be obtained. The intensity of the action decreases as the number of chlorine atoms in the molecule increases.

On heating mono- or di-iodobenzene with ferric bromide, the iodine is entirely replaced, paradibromobenzene being formed in both cases.

T. H. P.

**Derivatives of Symmetrical Trichlorobenzene.** By C. LORING JACKSON and F. H. GAZZOLO (*Amer. Chem. J.*, 1899, **22**, 50—60).—1:3:5-*Trichloro-2-iodobenzene*, prepared from 2:4:6-trichloraniline (V. Meyer and Sudborough, *Ber.*, 1894, **27**, 3151) by means of the diazo-reaction, crystallises from alcohol in slender, white needles, melts at 55°, sublimes easily, and is apparently not acted on by concentrated mineral acids or alkalis; when warmed, however, with alcoholic sodium ethoxide, iodine is removed, and trichlorobenzene formed. In this respect, 1:3:5-trichloro-2-iodobenzene resembles the corresponding tribromiodobenzene (Jackson and Calvert, *Abstr.*, 1896, **i**, 473), and, like the latter, does not interact with boiling aniline, aqueous caustic soda, or ethylic sodiomalonate; when warmed, however, with a mixture of nitric and sulphuric acids, it gives rise to 1:3:5-trichloro-2:4-dinitrobenzene, iodine being liberated.

1:3:5-*Trichloro-2-bromobenzene*, prepared from 2:4:6-trichloraniline, crystallises from alcohol in white, radiating needles, melts at 64—65°, readily sublimes, and is not acted on by concentrated mineral acids; when warmed, however, with a mixture of sulphuric acid and nitric acid of sp. gr. 1.52, it yields 1:3:5-trichloro-2-bromo-4:6-dinitrobenzene, which crystallises from a mixture of alcohol and benzene in rhombic plates, melts at 175°, and readily sublimes. This, when warmed with aniline, gives rise to 2-bromo-4:6-dinitro-1:3:5-trianilidobenzene (Jackson and Bancroft, *Abstr.*, 1890, 982), whilst, left in contact with cold, alcoholic sodium ethoxide (3 mols.), it is converted into bromodinitrodiethoxybenzene [ $\text{OEt}_2 : \text{Br} : (\text{NO}_2)_2 = 1 : 3 : 2 : 4 : 6$  or  $1 : 5 : 2 : 4 : 6$ ], which crystallises from alcohol in white needles and melts at 81—82°; other products are also formed, but could not be isolated. The latter action is of interest, because it is the first observed by the authors in which a chlorine atom has been replaced by hydrogen under the influence of sodium ethoxide; as a rule, the chlorine atom remains unaltered, or is replaced by an ethoxyl group, or, in the case of ethylic sodiomalonate or ethylic sodacetoacetate, by the radicles of these compounds (compare Jackson and Boos, *Abstr.*, 1898, **i**, 517; Jackson and Soch, *Abstr.*, 1896, **i**, 370; Dittrich, *Abstr.*, 1890, 1418; Stieglitz, *Abstr.*, 1891, 455, and Jackson and Lamar, *Abstr.*, 1897, **i**, 29).

W. A. D.

**Comparative Study of the Three Dinitrobenzenes.** By C. A. LOBRY DE BRUYN and ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, **18**, 9—12. Compare *Abstr.*, 1894, **i**, 573).—An introduction to the succeeding paper. It is pointed out that in the case of the reaction there considered, the velocity is greatest for the para-, and least for the meta-compound; this type of reaction is complementary to the two enumerated by Menschutkin (*Abstr.*, 1898, 187).

C. F. B.

Velocity of Substitution of a Nitro-group in Ortho- and Para-dinitrobenzene by Alkoxy. By ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, 18, 13—40).—The velocity of the reaction was determined by dissolving a weighed quantity of dinitrobenzene in so much alcohol that the concentration of the former was about equal to that which it would have in the gaseous state, adding some alcoholic sodium alkoxide, usually the equivalent quantity, allowing the whole to remain at either 25°, 35°, or 45°, removing a portion at intervals, acidifying this with an excess of acetic acid, and titrating the excess of the latter. The reaction takes place according to the equation  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{NaOR} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OR} + \text{NaNO}_2$  [ $\text{R} = \text{Me}, \text{Et}$ ]; in the case of metadinitrobenzene, however, no such replacement occurs, reduction to dinitrazoxybenzene taking place instead. The coefficient of velocity,  $k$ , was calculated by means of the equation  $-dc/dt = kc^2$ , where  $c$  = the concentration, and the following values were obtained :

	Sodium Ethoxide.		Sodium Methoxide.	
	Ortho.	Para.	Ortho.	Para.
25°.....	0·0260	0·211	0·0170	0·0442
35 .....	0·0786	0·707	0·0484	0·143
45 .....	0·233	2·21	0·139	0·474

The coefficient of increase of velocity with temperature,  $A$ , was also calculated by means of the equation  $d \log k/dT = A/T^2$ .

The rate of the reaction is greater with the para- than with the ortho-compound: 8·1—9·5 times as great with sodium ethoxide, 2·6—3·6 times with the methoxide. With sodium ethoxide, it is greater than with sodium methoxide:  $1\frac{1}{2}$  times as great with the ortho-, 5 times with the para-compound; this ratio is independent of the temperature. The temperature coefficient is in all cases about 2; rather greater for the para-, rather less for the ortho-compound. In the case of the ortho-compound, it was also found that the value of the constant is not affected by an excess of either reacting substance, or by dilution, or by the addition of a sodium salt (acetate or nitrite).

In the case of the analogous reaction,  $\text{CH}_3\text{I} + \text{NaOC}_2\text{H}_5 = \text{CH}_3 \cdot \text{OC}_2\text{H}_5 + \text{NaI}$ , it was found, on the other hand, that the constant increases slightly with the dilution, and is diminished slightly by the addition of sodium iodide. The latter result escaped the notice of Hecht, Conrad, and Brückner (*Abstr.*, 1890, 1046), because they operated with stronger solutions, in which the effect is less apparent.

C. F. B.

Influence of Water on the Velocity of Transformation of Orthodinitrobenzene by Sodium Methoxide and Ethoxide. By C. A. LOBRY DE BRUYN and ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, 18, 41—71).—The experiments were performed at 25° in the same way as when the pure alcohols were used as the solvents (preceding abstract), only, instead of these, the alcohols diluted with water in varying proportions were employed. Moreover, a certain quantity of nitrophenoxide is formed when dilute alcohol is employed, and this was estimated by a colorimetric method; presumably, it results from the action on the dinitrobenzene of sodium hydroxide

formed by the action of the water on the alkoxide:  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + 2\text{NaOH} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{ONa} + \text{NaNO}_2 + \text{H}_2\text{O}$ . As in the experiments with the pure alcohols, the velocity of transformation was found to be constant in each experiment; the values of the constant are tabulated below, along with the amounts of sodium nitrophenoxide formed, expressed as mols. of nitrophenetol or nitranisole per mol. of sodium nitrophenoxide; the strength of the alcohol is expressed as percentage by weight.

Strength of alcohol.....	100	98	96	94	92	90	80	70	60.	50
Constant $\times 10^4$ { Ethylic. Methylic.	260 169	240 172	225 —	211 —	198 —	189 182	153 197	124 209	112 225	104 249
Mols. alkoxy-com- pound per mol. phenoxide. { Ethylic. Methylic.	$\infty$ $\infty$	— —	— —	— —	— —	51 —	35 209	27 176	24.5 170	21 146

It will be seen that the addition of water diminishes the velocity of the reaction when ethylic alcohol is the solvent, increases it when the solvent is methylic alcohol. The amount of sodium phenoxide formed is always relatively small, and five times as small with the methylic as with the ethylic compound. In each experiment, the relation between the amounts of alkoxy-compound and phenoxide formed was found to remain constant throughout the experiment; from this fact, the conclusion is drawn, after consideration of various alternatives, that the relation in question also expresses the relation between the amounts of sodium alkoxide and hydroxide present in the solution, from the action of which on the dinitrobenzene the alkoxy-compound and the phenoxide are formed respectively. If this be so, then a sodium alkoxide is by no means so easily decomposed by water (into alcohol and sodium hydroxide) as is commonly supposed, for the above table would then show that when sodium ethoxide is dissolved in ethylic alcohol diluted with an equal weight of water (the case where the greatest amount of decomposition was observed), only about 5 per cent. of it is so decomposed. No determinations of the constant of velocity could be made with more dilute alcohols, owing to the too small solubility therein of the dinitrobenzene; experiments were made, however, in which the dinitrobenzene was boiled with the equivalent quantity of NaOH, dissolved in the dilute alcohol, until it had disappeared (8 or 16 hours), when the percentage that had been converted into alkoxy-compound was estimated, the rest having yielded phenoxide. The results were as follows:

Strength of Alcohol .....	40	20	10
Percentage converted { Ethylic .....	63	35	—
into alkoxy-compound { Methylic.....	96	88	70

Observations of other experimenters are cited in favour of the view that an alcoholic solution of sodium hydroxide contains alkoxide; the authors themselves find that when sodium hydroxide is dissolved in

absolute ethylic or methylic alcohol, the same velocity constant is obtained in the reaction with dinitrobenzene as when the alkoxide is used instead of the hydroxide.

Some solubilities, at different temperatures, of ortho- and para-dinitrobenzene in ethylic and methylic alcohols of various strengths are recorded in the paper.  
C. F. B.

**Preparation of Mixed Ethylic and Phenylic Phosphates.** By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 491—497. Compare this vol., i, 29, 264, 492).—These mixed phosphates are prepared by (i) the action of sodium ethoxide on the phenylic chlorophosphates; (ii) the action of sodium phenoxide on the ethylic chlorophosphates; (iii) the action of triphenylic phosphate on the alcohols and alkyl-oxides. By the action of alcohol on phenylic dichlorophosphate, *phenylic ethylic chlorophosphate*,  $\text{OEt} \cdot \text{PClO} \cdot \text{OPh}$ , is obtained; it is a colourless liquid which cannot be distilled; with water, it yields *phenylic ethylic phosphoric acid*,  $\text{HO} \cdot \text{PO}(\text{OEt}) \cdot \text{OPh}$ , as a colourless liquid. The *barium*, *lead*, and *sodium* salts are described.

Alcoholic ammonia reacts with phenylic ethylic chlorophosphate, yielding *phenylic ethylic phosphamide*,  $\text{NH}_2 \cdot \text{PO}(\text{OEt}) \cdot \text{OPh}$ ; it forms small, white crystals melting at  $133^\circ$ . Similarly, aniline yields *phenylic ethylic phosphanilide*, which crystallises from alcohol in white needles melting at  $143^\circ$ .  
R. H. P.

**Phenylic Chlorocarbonates.** By ETIENNE BARRAL and ALBERT MOREL (*Compt. rend.*, 1899, 128, 1578—1581).—Good yields of phenylic chlorocarbonates are obtained by the action of phosgene on the phenol in a sealed tube or on the aqueous sodium phenoxide. By this means, the chlorocarbonates from phenol, ortho- and para-cresols, guaiacol, thymol, trichlorophenol, tribromophenol, and pentachlorophenol have been prepared, the last two, however, giving only poor yields. In the case of  $\alpha$ - and  $\beta$ -naphthols, the method fails, as the alkali naphthoxides are completely decomposed by phosgene and water into sodium carbonate and naphthol.  
T. H. P.

**Synthesis of Phenyltribromomethylcarbinol and its Reactions.** By K. SIEGFRIED (*Chem. Centr.*, 1899, i, 606; from *J. Russ. Chem. Soc.*, 1898, 30, 914—920).—*Phenyltribromomethylcarbinol*, prepared in a similar way to the chloro-compound by Jocitsch's method (*J. Russ. Chem. Soc.*, 1897, 29, 97), crystallises from light petroleum in white needles, melts at  $78$ — $78.5^\circ$ , is easily soluble in ether, soluble in light petroleum or hot water, and rather sparingly so in cold water. The *acetate* crystallises from benzene in large, refractive plates, melts at  $140^\circ$ , is easily soluble in alcohol, ether, or benzene, and soluble in light petroleum or cold water. The results of a crystallographic examination of the acetates of the chloro- and bromo-compounds by P. A. Semjatschensky are given in the original paper; both substances form monoclinic crystals. Although Jocitsch (*loc. cit.*) readily obtained phenylchloracetic acid by the action of potassium hydroxide solution on phenyltrichloromethylcarbinol, the bromo-compound, when treated with a 10 per cent. aqueous solution of potassium hydroxide, yields benzaldehyde, bromoform, and mandelic acid, only a very small

quantity of phenylbromacetic acid, mixed with a little mandelic acid, being formed when the process is carried out with great care.

When phenyltribromomethylcarbinol is distilled under 25 mm. pressure, and the temperature rises above  $110^{\circ}$ , hydrogen bromide is liberated, and dibromacetophenone, together with some bye-products, are formed.

E. W. W.

**Action of Zinc Dust on Alcoholic Solutions of  $\alpha$ -Halogen-substituted Alcohols, and of Zinc Shavings on Alcoholic Solutions of their Acetates.** By ŽIVOJIN JOCITSCH (*Chem. Centr.* 1899, i, 606—607; from *J. Russ. Chem. Soc.*, 1898, 30, 920—924).—By boiling acetonechloroform with alcohol and zinc dust, isobutylene is liberated, and the oil obtained by treating the product with water yields isocrotylic chloride boiling at  $67$ — $69^{\circ}$  and dichlorisobutylene boiling at  $107$ — $109^{\circ}$ . When phenyltrichloromethylcarbinol is similarly treated, two main fractions are obtained. The one, a colourless liquid of a pleasant odour, boils at  $144$ — $145^{\circ}$ , and contains styrene, as, when treated with bromine, it forms a crystalline compound which melts at  $75^{\circ}$ . The second fraction boils at  $195$ — $197^{\circ}$ , and is chlorostyrene. Phenyltribromomethylcarbinol, under similar conditions, yields styrene and bromostyrene. The reaction with zinc dust takes place in three stages, the first consisting in the removal of the elements of hypochlorous or hypobromous acid, and the second and third in the reduction of the di-halogenised, unsaturated hydrocarbon so formed, with liberation of hydrogen bromide. The elimination of the elements of hypochlorous or hypobromous acid is probably effected by the formation of intermediate organo-zinc compounds, which react with water in a similar way to the zinc alkyls.

E. W. W.

**Retardation of Chemical Reactions due to Stereochemical Influences. II. Hydroxybenzylic Bases.** By CARL PAAL and FRIEDR. HÄRTEL (*Ber.*, 1899, 32, 2057—2062. Compare this vol., i, 587).—The authors have studied the action of acetic anhydride on the three isomeric orthohydroxybenzyl-nitranilines prepared by the condensation of saligenin with the three nitranilines (compare Paal and Senninger, *Abstr.*, 1894, i, 450). Orthohydroxyorthonitraniline is acted on by acetic anhydride only when the two are boiled together for some time, and the product formed is a monacetyl derivative, orthacetoxymethylorthonitraniline. Orthohydroxybenzylmetanitraniline and the corresponding para-compound, when boiled with acetic anhydride, both yield diacetyl derivatives; with the meta-compound, it is necessary to boil the mixture for some time, as otherwise a monacetyl derivative, orthohydroxymetanitracetanilide, is formed.

*Orthohydroxybenzylorthonitraniline*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystallises in dark red plates or flat needles, melts at  $125^{\circ}$ , is readily soluble in acetone, chloroform, or benzene, and also in alkalis; its sodium derivative is thrown down as a red, crystalline precipitate on the addition of concentrated sodium hydroxide. *Orthacetoxymethylorthonitraniline* crystallises in yellow needles melting at  $93^{\circ}$ , and is soluble in ether, but not in light petroleum, or cold alkalis. *Orthohydroxymetanitraniline* crystallises from alcohol in glistening,

yellow needles melting at  $115^{\circ}$ . *Orthohydroxybenzylmetanitracetanilide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NAc}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , crystallises in nearly colourless prisms melting at  $126^{\circ}$ , and is readily soluble in alcohol, benzene, chloroform, or alkalis. *Orthacetoxylbenzylmetanitracetanilide* crystallises in colourless, compact, concentrically arranged needles melting at  $99^{\circ}$ , and is readily soluble in alcohol, chloroform, or benzene, but insoluble in alkalis. *Orthohydroxybenzylparanitraniline* can only be obtained in small quantities by heating together an intimate mixture of the two constituents for 10–15 minutes at  $150\text{--}160^{\circ}$ ; it crystallises in golden, glistening plates melting at  $138^{\circ}$ , and is readily soluble in most solvents with the exception of light petroleum. *Orthacetoxylbenzylparanitracetanilide* crystallises in colourless needles melting at  $79^{\circ}$ ; a monacetyl derivative could not be obtained.

*Orthohydroxybenzylacetanilide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NAcPh}$ , crystallises in colourless needles melting at  $132^{\circ}$ . *Orthacetoxylbenzylacetanilide*,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NAcPh}$ , crystallises in long, colourless plates melting at  $98\text{--}99^{\circ}$ . J. J. S.

**Trimethylenimine.** By CURTIS C. HOWARD and WILHELM MARCKWALD (*Ber.*, 1899, 32, 2031–2035. Compare Gabriel and Weiner, *Abstr.*, 1888, 1292; Ladenburg and Sieber, *Abstr.*, 1890, 1394).—Trimethylenimine can be prepared in quantity and in a pure state by the action of sodium on a solution of paratoluenesulphotrimethylenimine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{N}<\text{CH}_2>\text{CH}_2$ . It boils at  $63^{\circ}$  under 748 mm.

pressure, fumes in the air, smells of ammonia, and has a sp. gr. 0.8436 at  $20.4^{\circ}$ . The base is unstable in presence of acids, and when warmed with dilute hydrochloric acid is converted into  $\gamma$ -chloropropylamine and its decomposition products. *Unsymmetrical trimethylenecarbamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NC}_3\text{H}_6$ , prepared by the action of cyanic acid on the base, crystallises in tablets, dissolves readily in water and slightly in alcohol, but not in ether, and melts at  $207^{\circ}$ . *Trimethylenimine trimethylenethiocarbamate*,  $\text{C}_3\text{H}_6\text{N}\cdot\text{CS}\cdot\text{SH}\cdot\text{NC}_3\text{H}_6$ , prepared by the action of carbon bisulphide on an ethereal solution of the base, separates in white crystals, dissolves readily in alcohol, and slightly in benzene, but not in ether, and melts at  $89^{\circ}$ . *Trimethylenephénylthiocarbamide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NC}_3\text{H}_6$ , prepared by the action of phenylthiocyanate on the base, dissolves readily in alcohol or benzene and slightly in light petroleum, and melts at  $110^{\circ}$ . *Benzenesulphotrimethylenimine*,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NC}_3\text{H}_6$ , dissolves slightly in water or light petroleum in the cold, but readily in alcohol or benzene, and melts at  $68^{\circ}$ . *Nitrosotrimethylenimine*,  $\text{NO}\cdot\text{NC}_3\text{H}_6$ , is a pale yellow, oily liquid, miscible with water, and boils at  $196\text{--}197^{\circ}$ . T. M. L.

**Constitution of Vinylamine.** By CURTIS C. HOWARD and WILHELM MARCKWALD (*Ber.*, 1899, 32, 2036–2038).—*Benzenesulphodimethylenimine*,  $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NC}_3\text{H}_6$ , prepared by the action of benzenesulphonic chloride on dimethylenimine (vinylamine), is a colourless, heavy oil insoluble in alkalis. *Paratoluenesulphodimethylenimine*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NC}_3\text{H}_6$ , crystallises from light petroleum, dissolves readily in alcohol, but only slightly in water, and melts at  $52^{\circ}$ .

The formation of these compounds proves the base to be secondary and not primary, and it must therefore be regarded as dimethylenimine,  $\text{NH} \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , and not as vinylamine,  $\text{CH}_2\text{:CH}\cdot\text{NH}_2$ . This conclusion is confirmed by a comparison of the boiling points of the series,

		Diff.
Dimethylenimine .. . . .	55—56° (756 mm.)	} 7·5°
Trimethylenimine.....	63 (748 mm.)	
Pyrrolidine .....	87·5—88·5	} 25
Piperidine.....	105—107	
		} 18

the differences among the polymethylenecarboxylic acids being 8°, 23·5°, and 18·5° for the first four members of the series. T. M. L.

**Bistrimethylenedi-imine.** By CURTIS C. HOWARD and WILHELM MARCKWALD (*Ber.*, 1899, 32, 2038—2042).—The bistrimethylenedi-paratoluenesulphonimide,  $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{N} \begin{smallmatrix} \text{C}_3\text{H}_6 \\ | \\ \text{C}_3\text{H}_6 \end{smallmatrix} \text{N}\cdot\text{SO}_2\text{C}_7\text{H}_7$ , recently described (this vol., i, 289), can be prepared by the action of trimethylenic bromide on the sodium salt of *diparatoluenesulphotrimethylenediamide*,  $\text{C}_3\text{H}_6(\text{NH}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2$ ; this substance dissolves readily in hot alcohol or benzene, and melts at 148°. *Bistrimethylenedi-imine*,  $\text{NH} \begin{smallmatrix} \text{C}_3\text{H}_6 \\ | \\ \text{C}_3\text{H}_6 \end{smallmatrix} \text{NH}$ , prepared from the toluenesulphonic acid derivative by hydrolysis with 25 per cent. hydrochloric acid, is a thick, colourless liquid which boils at 186—188°, has a faint ammoniacal odour, fumes in the air, and solidifies in ice to a crystalline mass which melts at 14—15°. The *platinochloride*,  $\text{C}_6\text{H}_{14}\text{N}_2\cdot\text{H}_2\text{PtCl}_6$ , melts with decomposition at 259°; the *aurichloride*,  $\text{C}_6\text{H}_{14}\text{N}_2\cdot 2\text{HAuCl}_4$ , melts at 216°; the *picrate*,  $\text{C}_6\text{H}_{14}\text{N}_2\cdot 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , forms long, slender needles and melts and decomposes at 226°. *Bistrimethylenedibenzimide* forms white crystals which are insoluble in water, but dissolve readily in hot alcohol or benzene, and melt at 124°.

*Ethylenediparatoluenesulphonamide*,  $\text{C}_2\text{H}_4(\text{NH}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)_2$ , crystallises from acetic acid, dissolves readily in hot alcohol or benzene, and melts at 159·5—160·5°. *Trimethylenethylenediparatoluenesulphonimide*,  $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{N} \begin{smallmatrix} \text{C}_2\text{H}_4 \\ | \\ \text{C}_3\text{H}_6 \end{smallmatrix} \text{N}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ , crystallises from absolute alcohol, dissolves readily in hot benzene or acetic acid, and melts at 150—151°. Trimethylenethylenedi-imine (compare Bleier, this vol., i, 664) melts at 42° and boils at 167° under 764 mm. pressure. T. M. L.

**History of Diazonium Salts.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 2043—2046).—A reply to Hantzsch (this vol., i, 685). It is pointed out that not a single chemist used the Blomstrand diazonium formula until 1894, when the author brought forward reasons for accepting it, based mainly on the physical properties of the salts (*Abstr.*, 1895, i, 134, 215, and 274). Hantzsch's physico-chemical researches on these compounds merely confirm what was previously known regarding them, and introduce no new factors. J. J. S.



**Orthodinitroso-derivatives of the Benzene Series.** By THEODOR ZINCKE and PH. SCHWARZ (*Annalen*, 1899, 307, 28—49. Compare Abstr., 1896, i, 429).—This paper contains experimental details relating to the summary which has already appeared (*loc. cit.*).

*Phenylenefurazan*,  $C_6H_4 \begin{smallmatrix} N \\ \diagup \diagdown \end{smallmatrix} O$ , the anhydride of benzeneorthodioxime, is obtained when the latter is distilled with dilute caustic soda; it crystallises from alcohol in long, white needles, and melts at 55°.

1 : 3 : 4-*Nitrotolylhydrazine* crystallises from hot water in deep red needles and melts at 110—111°; the hydrochloride forms golden-yellow leaflets.

*Nitrodiazotolueneimide* [ $Me : NO_2 : N_3 = 1 : 3 : 4$ ], prepared by the action of nitrous acid, crystallises from benzene in long needles or thickened plates, and melts at 35°; at the temperature of the water-bath, it is converted into orthodinitrosotoluene [ $Me : (NO)_2 = 1 : 3 : 4$ ].

*Toluenedioxime* [ $Me : (NOH)_2 = 1 : 3 : 4$ ] crystallises from hot water in small, yellowish-brown needles, and melts at 127—128°; 1 : 3 : 4-*tolylenefurazan* is very volatile, and crystallises from dilute alcohol in long, white needles melting at 37°.

*Nitrodiazotolueneimide* [ $Me : N_3 : NO_2 = 1 : 2 : 3$ ], prepared by the action of ammonia on the diazoperbromide derived from 1 : 2 : 3-nitrotoluidine, crystallises from alcohol and melts at 50°. *Toluenedioxime* [ $Me : (NOH)_2 = 1 : 2 : 3$ ] melts and decomposes at 140°, and when distilled with aqueous alkali, yields 1 : 2 : 3-*tolylenefurazan*, which melts at 44°.

*Nitrodiazometaxylenimine* [ $Me_2 : N_3 : NO_2 = 1 : 3 : 4 : 5$ ] melts at 66°. *Metaxylenedioxime* [ $Me_2 : (NOH)_2 = 1 : 3 : 4 : 5$ ] melts and decomposes at 142°; elimination of water gives rise to 1 : 3 : 4 : 5-*metaxylylenefurazan*, which crystallises from dilute alcohol in long, white needles, and melts at 60°. M. O. F.

**Nitro-derivatives of Orthodinitrosobenzene.** By P. DROST (*Annalen*, 1899, 307, 49—69).—*Orthonitrorthodinitrosobenzene* [ $NO_2 : (NO)_2 = 1 : 2 : 3$ ], obtained from orthodinitrosobenzene and nitric acid when excess of the latter is avoided, crystallises from glacial acetic acid in thin, yellow leaflets, and melts at 143°.

Fuming nitric acid converts it into *metadinitrorthodinitrosobenzene* [ $(NO_2)_2 : (NO)_2 = 1 : 3 : 4 : 5$ ], which crystallises in yellow needles and melts at 172°; the *potassium* derivative forms lustrous, golden leaflets, containing  $\frac{1}{2}H_2O$ , and the *sodium*, *silver*, and *ammonium* derivatives are well-defined. The additive compound with naphthalene crystallises from alcohol in long, red needles, and melts and decomposes at 172°. The *anilide*,  $NHPh \cdot C_6H(NO_2)_2(NO_2H)_2$ , obtained by heating dinitrodinitrosobenzene with aniline in alcohol, forms a red, crystalline powder, which blackens and detonates when heated; the *potassium* and *ammonium* derivatives yield red crystals, and the *aniline* compound forms a reddish-brown powder, which detonates when heated. When *metadinitrorthodinitrosobenzene* is reduced with tin and hydrochloric acid at common temperatures, 1 : 2 : 3 : 5-tetramidobenzene is obtained.

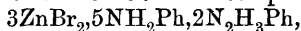
*Dinitrodiazobenzeneimide* [ $(NO_2)_2 : N_3 = 1 : 3 : 4$ ], prepared by the

action of ammonia on the diazoperbromide derived from dinitraniline, and by nitrating orthonitrobenzenediazoimide or paranitrobenzenediazoimide, crystallises from dilute acetic acid in pale yellow needles melting at  $69^{\circ}$ . *Paranitroorthodinitrosobenzene*  $[\text{NO}_2 : (\text{NO})_2 = 1 : 3 : 4]$ , obtained by heating the dinitro-imide on a water-bath, crystallises from a mixture of benzene and light petroleum in plates which contain benzene; it melts at  $72^{\circ}$ .

*Symmetrical orthodinitroorthodinitrosobenzene*  $[(\text{NO}_2)_2 : (\text{NO})_2 = 1 : 2 : 4 : 5]$ , produced on dissolving paranitroorthodinitrosobenzene in fuming nitric acid, separates from nitric acid of sp. gr. 1.4 in small, pale yellow crystals which melt at  $172^{\circ}$ , evolving brown gas; the *dianilide* forms dark red, slender needles, and melts at  $168^{\circ}$ . Symmetrical tetramidobenzene is obtained on reducing the dinitro-dinitroso-derivative with tin and hydrochloric acid.

*Orthonitrophenylenefurazan*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{O}$ , prepared from phenylenefurazan and fuming nitric acid, forms small, pale yellow crystals, and melts at  $98^{\circ}$ ; reduction with tin and hydrochloric acid converts it into 1 : 2 : 3-triamidobenzene. M. O. F.

**Combination of Phenylhydrazine and other Bases with Metallic Salts.** By JOSEPH MOITESSIER (*Compt. rend.*, 1899, 128, 1336—1337).—Compounds of metallic salts with phenylhydrazine and other bases can be obtained by mixing saturated alcoholic solutions of the proximate constituents in the proper proportions. As a rule, the compounds crystallise well, and are only slightly soluble in water or alcohol. The compound  $\text{ZnI}_2 \cdot \text{NH}_2\text{Ph} \cdot 2\text{N}_2\text{H}_3\text{Ph}$  forms needles which melt at  $180^{\circ}$ , and rapidly decompose at a slightly higher temperature; they are soluble in ether or alcohol. The compound



forms long, silky, curved needles; the compound  $\text{NiSO}_4 \cdot \text{NH}_2\text{Ph} \cdot 2\text{N}_2\text{H}_3\text{Ph} + 2\text{H}_2\text{O}$  is a greenish-white, crystalline powder insoluble in ether; the compound  $2\text{Cd}(\text{NO}_3)_2 \cdot 3\text{NH}_2\text{Ph} \cdot 5\text{N}_2\text{H}_3\text{Ph}$  melts and decomposes at  $195^{\circ}$ , and is insoluble in ether; the compound  $\text{ZnI}_2 \cdot \text{C}_{10}\text{H}_7 \cdot \text{NH}_2 \cdot 2\text{N}_2\text{H}_3\text{Ph}$  forms long, prismatic needles which melt and decompose at  $115^{\circ}$ , and are soluble in ether or alcohol, whilst the corresponding  $\beta$ -naphthylamine compound,  $3\text{ZnI}_2 \cdot 2\text{C}_{10}\text{H}_7 \cdot \text{NH}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ , decomposes at  $155^{\circ}$ , and is soluble in ether or alcohol, but only slightly soluble in benzene or chloroform.

If any of these compounds is treated with excess of Fehling's solution, the phenylhydrazine is decomposed and the other organic base is liberated, and can be extracted with ether (compare Abstr., 1898, i, 132, 133, and 413). C. H. B.

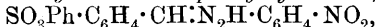
**New Coloured Phenylhydrazones.** By MARIUS ROUGY (*Bull. Soc. Chim.*, 1899, [iii], 21, 593—597).—*Orthonitrobenzaldehyde metanitrophenylhydrazone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , prepared by heating in alcoholic solution molecular proportions of metanitrophenylhydrazine and orthonitrobenzaldehyde, separates from alcohol in small, red crystals melting at  $203^{\circ}$ , and is soluble in benzene or ether, but insoluble in light petroleum.

*Metanitrobenzaldehyde metanitrophenylhydrazone* separates from

alcohol in small, maroon crystals melting at  $209^{\circ}$ , and dissolves in ether or benzene, but is insoluble in light petroleum.

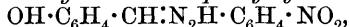
*Paranitrobenzaldehyde metanitrophenylhydrazone* separates from alcohol in small, red crystals melting at  $216^{\circ}$ , and is soluble in ether or benzene, but insoluble in light petroleum.

*Orthosulphobenzaldehyde metanitrophenylhydrazone*,



obtained by the interaction at ordinary temperatures of molecular proportions of an 8 per cent. solution of sodium orthobenzaldehydesulphonate and a solution of metanitrophenylhydrazine made faintly acid with acetic acid, separates from alcohol in orange-yellow crystals which dye wool orange-yellow.

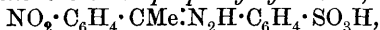
*Orthohydroxybenzaldehyde metanitrophenylhydrazone*,



forms small, maroon crystals melting at  $76^{\circ}$ , and is soluble in alcohol, ether, or benzene, but insoluble in light petroleum.

*Metanitracetophenone phenylhydrazone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe}\cdot\text{N}_2\text{HPh}$ , separates from alcohol in small, orange crystals melting at  $126^{\circ}$ , and is soluble in alcohol, ether, or benzene, but insoluble in light petroleum.

*Metanitracetophenone orthosulphophenylhydrazone*,



forms small, yellow crystals, and, in acid solution, dyes wool a beautiful yellow, resembling that given by auramine.

*Metanitrophenylpyrazolone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$ , prepared by the

interaction of molecular proportions of metanitrophenylhydrazine and ethylic acetoacetate, separates from alcohol in beautiful, maroon crystals melting at  $119^{\circ}$ , and is soluble in ether or benzene, but insoluble in light petroleum.

T. H. P.

### Orthochlorobenzhydroximic Chloride and its Derivatives.

By ALFRED WERNER and C. BLOCH (*Ber.*, 1899, 32, 1975—1985. Compare this vol., i, 690).—*Orthochlorobenzaldoxime* separates from alcohol in thick needles, and from water in thread-like crystals, and melts at  $75$ — $76^{\circ}$ . *Orthochlorobenzhydroximic chloride*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CCl}\cdot\text{NOH}$ , was obtained as a thick oil which could not be distilled, but occasionally deposited crystals melting at  $55$ — $56^{\circ}$ ; the oil appears to be a mixture of the two stereoisomerides. *Orthochlorobenzenylamidoxime*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{NH}_2)\cdot\text{NOH}$ , melts at  $117^{\circ}$ , crystallises from hot water in needles, and from alcohol in stout prisms, dissolves readily in ether, benzene, light petroleum, or acetic acid, as well as in acids or caustic alkalis; the *hydrochloride* crystallises in small needles, melts at  $225^{\circ}$ , and dissolves readily in water or alcohol, but not in other organic solvents; the *nitrate* separates from the aqueous solution in small needles and melts at  $237^{\circ}$ . The *benzoate* crystallises from hot alcohol in needles and melts at  $162^{\circ}$ ; it is soluble in dilute acids, but not in water or alkalis, and dissolves readily in ether, alcohol, or acetic acid, but only slightly in light petroleum or benzene. On fusing the benzoate or boiling its alcoholic solution, it gradually loses water, and is converted into *orthochlorobenzenylazoxime*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C} \begin{smallmatrix} \text{N}:\text{CPh} \\ \text{N}-\text{O} \end{smallmatrix}$ ; this

crystallises in white needles, melts at  $165^{\circ}$ , and dissolves readily in ether or acetic acid, but only slightly in benzene, light petroleum, or alcohol. *Orthochlorobenzenzylanilidoxime*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{NHPh})\cdot\text{NOH}$ , crystallises from dilute alcohol in silky needles, melts at  $140^{\circ}$ , dissolves in acids or alkalis, and is readily soluble in ether or alcohol, but only slightly in water, light petroleum, or acetic acid. *Orthochlorobenzenzyltoluidoxime*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})\cdot\text{NOH}$ , crystallises from alcohol in needles and melts at  $173^{\circ}$ . *Orthochlorobenzenzylpiperidoxime*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{C}_5\text{NH}_{10})\cdot\text{NOH}$ , crystallises in well-formed, glistening rhombohedra and melts at  $165^{\circ}$ . *Orthodichlorodibenzenzylazoxime*,

$\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}\begin{smallmatrix} \text{N}:\text{C}\cdot\text{C}_6\text{H}_4\text{Cl} \\ \text{N}\cdot\text{O} \end{smallmatrix}$ , is produced by heating orthochlorobenzhydroximic chloride until the evolution of gas ceases; it crystallises from dilute alcohol in thread-like needles and melts at  $93^{\circ}$ . *Dichlorobenzil-dioxime peroxide*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_4\text{Cl}\cdot\text{C}:\text{N}\cdot\text{O} \\ \text{C}_6\text{H}_4\text{Cl}\cdot\text{C}:\text{N}\cdot\text{O} \end{smallmatrix}$ , is produced, together with a certain

amount of orthochlorobenzhydroxamic acid, on heating orthochlorobenzhydroximic chloride with dilute sodium hydroxide; it melts at  $131^{\circ}$ , crystallises from alcohol in needles, does not dissolve in acids or alkalis, or in water or light petroleum, but dissolves slightly in benzene and readily in ether, alcohol, or acetic acid. On reduction with zinc dust and acetic acid, it gives *orthodichlorobenzilsyndioxime*,  $\text{C}_2(\text{NOH})_2(\text{C}_6\text{H}_4\text{Cl})_2$ ; this crystallises from alcohol in needles and melts at  $226\text{--}227^{\circ}$ , dissolves readily in dilute alkalis, and in ether, alcohol, or benzene, but only slightly in light petroleum or acetic acid, and is insoluble in water. The *diacetate* crystallises in slender needles, melts at  $129^{\circ}$ , dissolves readily in alcohol or ether, and slightly in benzene; the *dipropionate* melts at  $97^{\circ}$ , and resembles the acetate; by heating with caustic potash, both are converted into

*diorthochlorophenylfuran*,  $\text{O}\begin{smallmatrix} \text{N}:\text{C}\cdot\text{C}_6\text{H}_4\text{Cl} \\ \text{N}:\text{C}\cdot\text{C}_6\text{H}_4\text{Cl} \end{smallmatrix}$ , which crystallises from alcohol in prisms, melts at  $107^{\circ}$ , and is insoluble in water, acids, or alkalis, but dissolves slightly in light petroleum and readily in ether, alcohol, acetic acid, or benzene. *Orthodichlorobenzilantidioxime* is produced on boiling an alcoholic solution of the syndioxime; it crystallises from benzene in microscopic needles, melts at  $270^{\circ}$ , dissolves readily in dilute alkalis and in ether or acetic acid, is slightly soluble in benzene, alcohol, or light petroleum, and insoluble in water. The *diacetate* melts at  $157^{\circ}$ , dissolves readily in alcohol or ether, slightly in benzene, and not at all in water, acetic acid, or light petroleum; the *dipropionate* crystallises from alcohol in colourless needles and melts at  $105^{\circ}$ ; both compounds are hydrolysed by dilute alkalis, giving back the antidioxime and not the furazan derivative.

T. M. L.

**Behaviour of Acetanilide in Solutions of Zinc Chloride and Hydrogen Peroxide.** By W. BRÄUTIGAM (*Chem. Centr.*, 1899, i, 560; from *Pharm. Zeit.*, 44, 75).—By the action of zinc chloride on acetanilide at  $180^{\circ}$ , the yellow dye flavaniline is formed, but acetanilide is not attacked by boiling with zinc chloride in aqueous solution or with hydrogen peroxide. By boiling an aqueous solution with

hydrogen peroxide and zinc chloride, however, a carmine red liquid is formed which, on further heating, becomes brownish-red and on cooling deposits a brownish-red powder which is insoluble in ether. This reaction is characteristic of acetanilide, for under similar conditions phenacetin gives only a yellowish coloration and antipyrine a yellowish precipitate. E. W. W.

**Derivatives of Metamidophenol.** By RICHARD E. MEYER and W. SUNDMACHER (*Ber.*, 1899, **32**, 2112—2124. Compare Abstr., 1878, 237; Ikuta, *ibid.*, 1893, i, 265).—A yield of some 70 per cent. of metamidophenol may be obtained by fusing metamidobenzene-sulphonic acid with sodium hydroxide (Germ. pat. 44792); it melts at 121—122° (Ikuta gives 122—123°) and readily forms azo-dyes.

*Metahydroxyphenylcarbamide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , obtained by mixing concentrated aqueous solutions of potassium cyanate and of metamidophenol hydrochloride, crystallises from boiling water in large, colourless prisms melting at 180—181° and readily soluble in alcohol, acetone, or acetic acid, but practically insoluble in benzene or light petroleum. When the carbamide is heated with aniline at 180—190°, ammonia is evolved and *metahydroxycarbanilide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , is formed; this crystallises in glistening, felted needles melting at 230—232°, and is only sparingly soluble in hot water. *Metadihydroxycarbanilide* (compare Struve and Radenhausen, Abstr., 1896, i, 35) is obtained when metahydroxyphenylcarbamide and metamidophenol are heated at 180—190°.

*Metahydroxyphenylthiocarbamide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , crystallises from water in large, colourless prisms melting at 183—184°.

*Metahydroxythiocarbanilide*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ , is obtained when an alcoholic solution of metamidophenol and phenylthiocarbimide is warmed on the water-bath for an hour and then allowed to remain for a day; it crystallises in glistening, pearly plates melting at 155—156°. *Metadihydroxythiocarbanilide*,  $\text{CS}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ , is formed when the amidophenol is boiled for about 15 hours with an alcoholic solution of rather more than the theoretical amount of carbon bisulphide; it crystallises from water in pale yellow needles melting at 164—165°, and is readily soluble in most organic solvents with the exception of benzene and light petroleum.

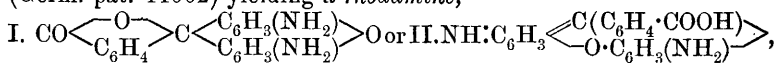
*Ethyl metahydroxyphenyloxamate*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{COOEt}$ , obtained in the same manner as the ortho- and para-compounds (Abstr., 1896, i, 367; 1898, i, 320), crystallises in thick, colourless needles melting at 183—184°; it is readily hydrolysed by warm dilute sodium hydroxide; the acid forms colourless, compact crystals melting and decomposing at 215°.

*Metahydroxyphenyloxamide*,  
 $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CONH}_2$ ,  
 crystallises in glistening needles melting at 225—227° and is readily soluble in alkalis.

*Metadihydroxydiphenyloxamide*,  $\text{C}_2\text{O}_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ , obtained by heating a mixture of ethyl oxalate and metamidophenol at 170° for half an hour, crystallises in colourless, glistening plates melting at 269—270°.

Phthalic anhydride can condense with either one or two molecular

proportions of alkylated metamidophenols, yielding respectively alkyl derivatives of metamidohydroxybenzoylbenzoic acid (Germ. pat. 85931) and rhodamines. Metamidophenol itself readily condenses with phthalic anhydride in the presence of concentrated sulphuric acid (Germ. pat. 44002) yielding a *rhodamine*,



which is isomeric with 2:7-diamidofluoran and with *i*-diamidofluoran (Meyer and Friedland, Abstr., 1898, i, 590). It crystallises in reddish-brown plates, begins to sinter at 230°, and melts at 250–252°, dissolves readily in methylic, ethylic, or amyl alcohol, in acetone or acetic acid, yielding reddish-yellow solutions with an intense green fluorescence, but is only sparingly soluble in benzene or ether, yielding colourless, non-fluorescent solutions; it is insoluble in light petroleum, but dissolves readily in mineral acids, and may be precipitated from such solutions on the addition of not too large a quantity of alkali. The *hydrochloride*,  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3 \cdot \text{HCl}$ , with the quinonoid structure II, crystallises in reddish-brown plates with a green metallic lustre; the *sulphate*,  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_3 \cdot \text{H}_2\text{SO}_4$ , crystallises in large, lustrous, green needles, and the *acetyl* derivative in yellow plates melting at 170–173°. When dissolved in hot dilute sulphuric acid and treated while still hot with sodium nitrite, rhodamine is converted into fluorescein.

Molecular proportions of metamidophenol and of phthalic anhydride in hot toluene condense in quite a different manner from alkylated metamidophenols and the same anhydride (*loc. cit.*), the product formed being *metahydroxyphthalamic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , which crystallises in minute, felted needles, melting at 227–229°, and fairly readily soluble in alcohol, ether, or acetic acid.

Most primary amines, when mixed with an acid anhydride, in molecular proportion and in the presence of an indifferent solvent, react in the same manner, the amido-group taking part in the condensation. Phthalic anhydride and aniline in toluene solution yield phthalanilic acid melting at 170°, with conversion into phthalanil, which then melts at 203° (Laurent and Gerhardt give 192°, Zincke 158°, and Thorp 191–193° as the melting point of the anilic acid). Benzoic anhydride and aniline, under similar conditions, yield benzoic acid and benzanilide; the same anhydride and metamidophenol yield benzoic acid and *meta*-hydroxybenzanilide (compare Ikuta, *loc. cit.*). J. J. S.

**Aromatic Carbimides.** By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 586–593).—The authors have discovered a new method of preparing aromatic carbimides by which good yields of the pure products are readily obtained. This consists in treating a solution of the aromatic base in benzene with a solution of phosgene in toluene; one mol. of the carbimide is first formed along with two mols. of the hydrochloride of the base, and then, by prolonged heating in presence of excess of phosgene, this hydrochloride is converted into the carbimide. Thus by the action of phosgene on the nitranilines, 2-, 3-, and 4-nitrophenylcarbimides have been prepared, and from them the corresponding ethylic nitrophenylcarbamates.

*Metanitroparatolylcarbimide*, obtained by the action of excess of phosgene on metanitroparatoluidine, forms small, yellow needles melting at  $57-58^{\circ}$ , and is soluble in benzene, toluene, chloroform, or ether, but only dissolves slightly in cold light petroleum, although more so on heating.

*Ethyllic metanitroparatolylcarbamate*,  $[\text{Me}:\text{NO}_2:\text{NH}\cdot\text{COOEt}=1:3:4]$ , formed by the interaction of alcohol and the corresponding nitrocarbimide, in molecular proportion, crystallises from 95 per cent. alcohol in beautiful, amber-yellow, prismatic needles melting at  $63^{\circ}$ ; it is very soluble in benzene or ether, less so in light petroleum, and is insoluble in water in the cold, but dissolves appreciably on heating.

*5-Nitrorrhotolylcarbimide*,  $[\text{Me}:\text{NO}_2:\text{NCO}=1:5:2]$ , obtained from 5-nitrorrhotoluidine, crystallises in light yellow, microscopic needles melting at  $127^{\circ}$ , and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

*Ethyllic 5-nitrorrhotolylcarbamate*  $[\text{Me}:\text{NH}\cdot\text{COOEt}:\text{NO}_2=1:2:5]$  crystallises from alcohol in pale yellow needles melting at  $127^{\circ}$ , and is soluble in benzene, ether, or water, but almost insoluble in light petroleum.

*Paranitrorrhotolylcarbimide*, prepared from metanitrorrhotoluidine, crystallises in small, white needles melting at  $48-49^{\circ}$ , and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

*Ethyllic paranitrorrhotolylcarbamate* crystallises from alcohol in thin, white needles melting at  $129-130^{\circ}$ , and readily dissolves in benzene or ether, but is less soluble in light petroleum or water.

*Orthonitroparatolylcarbimide*, prepared from orthonitroparatoluidine, forms white prisms melting at  $49-50^{\circ}$ , and is soluble in benzene, toluene, ether, chloroform, or light petroleum.

*Ethyllic orthonitroparatolylcarbamate* separates from aqueous alcohol in the form of microscopic, pale yellow needles melting at  $77-78^{\circ}$ , fairly soluble in benzene or boiling water, less so in ether, and insoluble in light petroleum or cold water.

All these nitrotolylcarbamides are decomposed by the prolonged action of boiling water, carbonic anhydride being evolved and the corresponding carbamide and fundamental base formed. T. H. P.

**Nitration of Benzoic Acid and of its Methylic and Ethylic Salts.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1899, 18, 267—291).—The acid or ethereal salt (3 grams) was introduced in successive small quantities into five times the weight of pure nitric acid, the temperature of the latter being maintained constant within  $5^{\circ}$ ; the solution was allowed to remain for a quarter of an hour, and then poured into iced water (120 c.c.). In the case of the acids, the precipitate was filtered off, and the substance dissolved in the filtrate was recovered by extraction with ether; in the case of the alkylic salts, the product was extracted at once with ether, and hydrolysed by warming with normal alkali, the acids being afterwards extracted with ether. The yield was nearly equal to that calculated on the assumption that mononitro-products only were formed. The

proportions in which the meta-, ortho-, and para-isomerides were present in the product were determined by a method which is an improvement on that previously described (this vol., ii, 257). In order to estimate the amount of para-compound present, a weighed quantity of the product was shaken in a bottle at  $24.4^{\circ}$  with excess of the pure meta- and ortho-acid, and about 65 c.c. water; at the same time, a mixture of the pure meta- and para-acids only was shaken with water in the same way. From the first bottle, two portions of 25 c.c. were removed by means of a pipette furnished with a plug of cotton wool; pipette and plug were then rinsed back into the bottle with about 50 c.c. of water. From the second bottle, 25 c.c. were removed, and an equal amount of water added without special precaution; both solutions were then shaken again. Of the liquid removed from each bottle, 25 c.c. were titrated with  $N/20$  baryta; both solutions were saturated with meta- and ortho-acid, but that from the first bottle contained para-acid in addition, and consequently required more baryta; the difference in the amounts of baryta required multiplied by 2, is equivalent to the amount of para-acid present in the  $25 \times 2$  c.c. of solution removed from the first bottle. The process is continued until the solutions from both bottles require the same amount of baryta; all the para-acid has then been removed from the first bottle. The sum of the differences obtained in the successive pairs of titrations is equivalent to the total weight of para-acid present in the weight of the product operated on. In the case of the ortho- and meta-acids, which are much more soluble in water, the solubility of the other two acids was found to be affected by the amount of the ortho- or meta-acid which had dissolved, with the result that the amount of ortho-acid found came out too low, that of meta-acid too high; however, by making experiments in which different weighed quantities of each pure acid were shaken with excess of the other two acids in the manner described above, and comparing the amount found with that taken, it was possible to ascertain the correction to be applied to any quantity found by the experiment. In the actual experiments, the amounts of para- and ortho-compounds only were estimated as described; that of the meta-compound was calculated by difference. In all cases, a correction had to be applied for a small amount of acid impurity introduced through the use of the ether; this was ascertained by shaking simultaneously with water (1) some of the product along with excess of pure meta-, ortho-, and para-acids, and (2) the mixture of the three pure acids only, in the manner described above, and noting the difference in the amounts of baryta solution required. In an experiment made to test the method, it was found that the absolute error in the determination of the amount of each isomeride was rather less than 1 (0.2—0.8) per cent. of the weight of the product operated upon.

The results of the determinations are recorded in the table; the numbers express the percentage of each isomeride in the product of nitration. The temperature of  $-30^{\circ}$  was obtained by means of a mixture of solid carbonic anhydride and 95 per cent. alcohol contained in a vessel jacketed with pure, dry wool.



Nitration at		- 30° (- 40° for Ethyl benzoate)	0°	+ 30°
Benzoic acid	{ ortho .....	14.4	18.5	22.3
	{ meta .....	85.0	80.2	76.5
	{ para .....	0.6	1.3	1.2
Methyl benzoate	{ ortho .....	23.6	21.0	25.7
	{ meta .....	74.4	73.2	69.8
	{ para .....	2.0	5.8(?)	4.5
Ethyl benzoate	{ ortho .....	25.5	28.3	27.7
	{ meta .....	73.2	68.4	66.4
	{ para .....	1.3	3.3	5.9

It will be seen that in all cases the meta-compound remains the chief product of the nitration, but that the amount decreases as the temperature rises; in the case of benzoic acid itself, the amount of ortho-compound formed increases considerably with the temperature of nitration, whilst that of the para-compound increases but little; with its ethereal salts, the converse is the case. It appears further that, on the whole, successive substitution of the H of the COOH group by Me and Et occasions a gradual decrease of the amount of meta-compound formed and increase of the amounts of ortho- and para-compounds.

The formation of a para-derivative in the nitration of alkylic benzoates, unnoticed hitherto, was proved by isolating paranitrobenzoic acid from the product. C. F. B.

**Camphoric Acid.** VI. By WILLIAM A. NOYES (*Amer. Chem. J.*, 1899, 22, 1—5. Compare this vol., i, 284).—1 : 3 : 2-*Hexahydro-xylic acid* [ $\text{Me}_2 : \text{CO}_2\text{H} = 1 : 3 : 2$ ], prepared by reducing 2 : 6-dimethylbenzoic acid (*loc. cit.*) with sodium and amyl alcohol, crystallises from light petroleum or benzene, melts at 72°, boils at 250—252°, and is volatile with steam; on treatment with phosphorus pentachloride and bromine, it yields *α-bromohexahydro-xylic chloride*, which is not hydrolysed on boiling with water or 10 per cent. caustic soda, although it is readily decomposed when warmed with glacial formic acid, giving rise to *α-bromohexahydro-xylic acid*,  $\text{C}_9\text{H}_{15}\text{BrO}_2$ . This crystallises from formic acid in leaflets, melts at 150—151°, and, when warmed with alcoholic potash, yields  $\Delta^1$ -*tetrahydro-xylic acid*,  $\text{C}_9\text{H}_{14}\text{O}_2$ , which separates from light petroleum in compact crystals, melts at 89—90°, and is only slowly oxidised by potassium permanganate.

The properties given for  $\Delta^1$ -tetrahydro-xylic acid and the compounds from which it was obtained plainly indicate its non-identity with *cis*-campholytic acid; Collie's formula for camphoric acid (*Abstr.*, 1892, 864) is therefore no longer admissible. W. A. D.

***α*-Amido-acids.** By EMIL ERLÉNMEYER, jun. (*Annalen*, 1899, 307, 70—113).—This paper comprises a theoretical discussion of the author's previous work on the *α*-amido-acids, and of the results described in the following abstracts.

In a former paper (*Abstr.*, 1895, i, 281), the properties of phenyl-*α*-amidolactic acid were recorded. Another modification has been isolated from among the products of condensation of benzaldehyde and glycocine under the influence of caustic soda; it crystallises in small, white needles on adding absolute alcohol to the concentrated aqueous

solution, and melts at  $187-188^{\circ}$ , instead of  $196^{\circ}$ . The new acid contains  $1\text{H}_2\text{O}$ , and dissolves in 17 parts of water instead of 38 parts; the *copper* salt is pale blue, and dissolves in 255 parts of water instead of 2108 parts.

The relationship of the stereoisomeric diphenylhydroxyethylamines is considered at some length, and the following conclusions are drawn concerning the behaviour of amido-acids towards aldehydes. 1. The  $\alpha$ -methylenic group in amidocarboxylic acids undergoes condensation with aldehydes in presence of caustic soda. 2. The methylenic group in benzylamine is capable of undergoing the same change. 3. The double linking in the complex  $\text{COOH}\cdot\text{CH}\cdot\text{N}\cdot\text{CH}\cdot$  is capable of changing its position, giving rise to the group  $\text{COOH}\cdot\text{C}\cdot\text{N}\cdot\text{CH}_2$ . 4. The complex  $\text{COOH}\cdot\text{C}(\text{OH})\cdot\text{NH}\cdot\text{CH}\cdot\text{OH}$  can change into the group  $\text{COOH}\cdot\text{CH}\cdot\text{NH}\cdot\text{CO}$ , as illustrated by the formation of phenylacetyl-phenylalanine from phenylpyruvic acid and ammonia. M. O. F.

**The Two Stereoisomeric Diphenylhydroxyethylamine Bases.** By EMIL ERLÉNMEYER, jun. (*Annalen*, 1899, 307, 113—137. Compare Abstr., 1896, i, 305; 1897, i, 480, and foregoing abstract).—The *benzylidene* derivative of isodiphenylhydroxyethylamine,



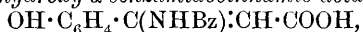
is prepared by exposing a mixture of glycocine dissolved in water, benzaldehyde in alcohol, and caustic soda in water, to direct sunlight during 10 hours, or to a temperature of  $55^{\circ}$  during 5 hours (compare Abstr., 1895, i, 596); it melts at  $134^{\circ}$ , and crystallises from alcohol in monoclinic needles [ $a:b:c=2\cdot22905:1:2\cdot1187$ .  $\beta=82^{\circ}8'$ ]. The *acetyl* derivative crystallises from alcohol and melts at  $117^{\circ}$ .

Hydrochloric acid resolves the benzylidene derivative into benzaldehyde and isodiphenylhydroxyethylamine, which melts at  $129-130^{\circ}$ , and crystallises from methylic alcohol in monoclinic plates [ $a:b:c=3\cdot3339:1:2\cdot2396$ .  $\beta=70^{\circ}15'$ ]. The hydrochloride melts and decomposes at  $211^{\circ}$ ; it crystallises from methylic alcohol in long, six-sided plates which contain 1 mol. of the solvent and belong to the triclinic system [ $a:b:c=0\cdot60151:1:1\cdot1631$ .  $\alpha=88^{\circ}42'$ ;  $\beta=119^{\circ}40'$ ;  $\gamma=90^{\circ}25'$ ].

Diphenylhydroxyethylamine is prepared according to the method of Goldschmidt and Polonowska by reducing benzoinoxime with sodium amalgam and glacial acetic acid (compare Söderbaum, Abstr., 1896, i, 98); it melts at  $163^{\circ}$ , and crystallises from alcohol in colourless, lustrous needles belonging to the monoclinic system [ $a:b:c=2\cdot1370:1:2\cdot8933$ .  $\beta=74^{\circ}23'$ ]. The hydrochloride crystallises from methylic alcohol in needles belonging to the hexagonal system; it contains 1 mol. of the solvent, and decomposes at  $234^{\circ}$ . When the base is heated at temperatures slightly above the melting point, it is resolved into benzylamine and benzaldehyde, a change which the isomeride also undergoes when submitted to similar conditions. M. O. F.

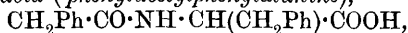
**Synthesis of Tyrosine.** By EMIL ERLÉNMEYER, jun., and JOHN T. HALSEY (*Annalen*, 1899, 307, 138—145. Compare Abstr., 1899, 30, 197).—The *lactimide*,  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{NBz} \\ \diagup \\ \text{CO} \end{smallmatrix}$ , prepared by heating

parahydroxybenzaldehyde, hippuric acid, anhydrous sodium acetate, and acetic anhydride during 10–15 minutes on the water-bath, crystallises from dilute alcohol in small, yellow needles, and melts at 172–173°. *Parahydroxy- $\alpha$ -benzamidocinnamic acid*,



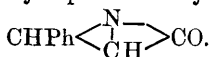
obtained on hydrolysing the lactimide with hot, aqueous, caustic soda, crystallises from dilute alcohol in white needles, and melts at 228–229°, when it decomposes; reduction with sodium amalgam in alkaline solution gives rise to benzoyltyrosine, which yields tyrosine under the influence of concentrated hydrochloric acid at 150°. M. O. F.

**Formation of Phenylacetylphenylalanine from Phenylpyruvic Acid and Ammonia.** By EMIL ERLMEYER, jun., and JULIUS KUNLIN (*Annalen*, 1899, 307, 146–162).— *$\alpha$ -Phenylacetamidophenylpropionic acid (phenylacetylphenylalanine)*,



is very sparingly soluble in hot water, crystallises from a mixture of benzene and alcohol in small, colourless needles, and melts at 126°; the *sodium* salt is sparingly soluble in water, and crystallises in aggregates of needles, whilst the *silver* salt is also sparingly soluble, and is sensitive towards light. The *amide* obtained by the action of ammonia either on phenylpyruvic acid or on  $\alpha$ -benzamidocinnamic acid, crystallises from hot alcohol in slender, colourless needles, and melts at 186°; the production of this compound from benzamidocinnamic acid is associated with formation of benzamide.

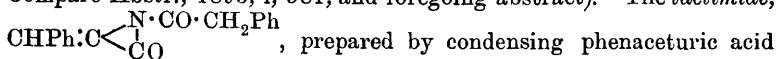
The amide just described is identical with the compound obtained by Plöchl (Abstr., 1886, 351), and first regarded by him as phenylamidolactic acid, but subsequently represented by the formula



Plöchl obtained the same substance from ammonia and phenylpyruvic acid, which he called phenylglycidic acid, but appears not to have recognised its identity with the compound from benzamidocinnamic acid and ammonia.

When phenylacetylphenylalanine is hydrolysed with concentrated hydrochloric acid at 150°, it is resolved into phenylalanine and phenylacetic acid; contrary to the statement of Plöchl, formic, benzoic, and  $\alpha$ -amidocinnamic acids are not formed. M. O. F.

**Synthesis of Phenylacetylphenylalanine.** By EMIL ERLMEYER, jun., and JULIUS KUNLIN (*Annalen*, 1899, 307, 163–170. Compare Abstr., 1893, i, 581, and foregoing abstract).—The *lactimide*,



with benzaldehyde under the influence of acetic anhydride and anhydrous sodium acetate, crystallises from alcohol in yellow plates and melts at 105°.

*Phenylacetamidocinnamic acid*,  $\text{CHPh} : \text{C}(\text{COOH}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ , produced when the lactimide remains in contact with water during several days, separates from alcohol in large, monoclinic crystals melting at 186° [ $a : b : c = 1.0428 : 1 : 0.69247$ .  $\beta = 68^\circ 3'$ ]. Reduction

with sodium amalgam converts it into  $\alpha$ -phenylacetamidophenylpropionic acid (phenylacetylphenylalanine). M. O. F.

[Tannins]. By HERMANN KUNZ-KRAUSE (*Chem. Centr.*, 1899, i, 559).—The paper contains a summary of the author's work on the classification of tannins.

Ferric chloride is a general reagent for tannins. Certain groups of tannins which are derived from two or more mols. of protocatechuic acid by elimination of water are also precipitated by gelatin, albumin alkaloids, potassium antimony tartrate, and other compounds. The reactions of these substances and others with gallic, digallic, trigallic, ellagic, ellagitannic, and chebulic acids, and also with hamamelitannin and tannin are tabulated. The reactions and decompositions which tannins undergo in the plants containing them, and particularly the formation of phlobaphens and "reds," are used, to some extent, as a basis for classification. The 'reds' are the red to reddish-brown colouring matters of the bark, which are formed in the same way as gallotannic acid by a process of dehydration of aromatic hydroxy-acids. The phlobaphens and reds are both precipitated by gelatin, and may be obtained from the respective tannins or tannogens by boiling with dilute sulphuric acid. E. W. W.

**Aniline Salts of the Phthalic Acids.** By CARL GRAEBE and J. BUENZOD (*Ber.*, 1899, 32, 1991—1995. Compare *Abstr.*, 1897, i, 60).—*Aniline 3-nitrophthalate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{COOH})_2 \cdot \text{NH}_2\text{Ph}$ , separates from alcoholic solution in bright yellow flakes and melts at  $180$ — $181^\circ$  with elimination of water; the product of decomposition melts at  $132$ — $133^\circ$ . The salt is insoluble in ether, but readily soluble in hot water; the normal salt is not formed even in presence of a large excess of aniline. No loss in weight occurs on heating at  $100^\circ$ , but at  $120$ — $130^\circ$  it loses water and aniline, and gives a mixture of a little nitrophthalic acid with *nitrophthalanil*; this is yellow, melts at  $134^\circ$ , is insoluble in water, but readily soluble in hot alcohol.

*Aniline 4-nitrophthalate* melts at  $181$ — $182^\circ$  with loss of water, the product of decomposition melting at  $186$ — $189^\circ$ . No loss of weight occurs on heating at  $90$ — $100^\circ$ , but at  $120$ — $130^\circ$  it is converted into *4-nitrophthalanil* together with a little nitrophthalic acid; the phthalanil crystallises from alcohol and melts at  $192^\circ$ .

*Aniline 4-hydroxyphthalate*,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{COOH})_2 \cdot \text{NH}_2\text{Ph}$ , crystallises in colourless flakes, dissolves moderately in hot water and readily in hot alcohol, melts at  $159^\circ$  with loss of water, and remelts at  $240^\circ$ . *4-Hydroxyphthalanil* is produced on heating the aniline salt to its melting point, or by prolonged heating at  $100^\circ$ ; it melts at  $251^\circ$ , is insoluble in water, but is slightly soluble in cold and readily so in hot alcohol.

*Aniline 4-chlorophthalate* melts at  $151^\circ$  and dissolves readily in hot alcohol. *4-Chlorophthalanil* is produced slowly on heating the aniline salt at  $100^\circ$  and rapidly at  $160$ — $170^\circ$ ; it melts at  $174^\circ$  and dissolves fairly readily in hot, but only slightly in cold alcohol.

Normal *aniline 3:4-dichlorophthalate*,  $\text{C}_6\text{H}_2\text{Cl}_2(\text{COOH})_2 \cdot 2\text{NH}_2\text{Ph}$ , melts and decomposes at  $163^\circ$ , dissolves readily in hot alcohol and hot water, but only slightly in the cold, and is only very slightly soluble

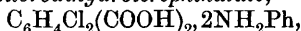
in ether. On heating at  $100^{\circ}$ , it loses 1 mol. of aniline, and at  $120$ — $130^{\circ}$  is converted into 3:4-chlorophthalanil, which melts at  $170$ — $171^{\circ}$  and is only slightly soluble in alcohol; a small amount of the dichlorophthalic acid is also produced.

Normal aniline tetrachlorophthalate melts at  $263^{\circ}$  and is insoluble in water or ether, but moderately soluble in hot alcohol. When heated at  $100^{\circ}$ , it loses water and a little aniline, and at  $120$ — $130^{\circ}$  it is converted completely into tetrachlorophthalanil melting at  $268$ — $269^{\circ}$ .

Aniline nitroterephthalate is a colourless salt very readily soluble in alcohol; when heated, it becomes yellow at  $145^{\circ}$  and melts at  $191^{\circ}$ ; when heated at  $120^{\circ}$ , it loses aniline and is converted completely into nitroterephthalic acid.

Normal aniline 2:5-dichloroterephthalate, forms colourless crystals which decompose at  $170$ — $175^{\circ}$  and melt at  $204$ — $205^{\circ}$ ; when heated at  $120^{\circ}$ , it loses aniline and is converted completely into dichloroterephthalic acid.

Normal aniline dichlorodihydroterephthalate,



melts at  $180^{\circ}$  and loses the whole of its aniline when heated at  $120^{\circ}$ .

Aniline 5-nitroisophthalate melts at  $165^{\circ}$ , remelts at  $192$ — $193^{\circ}$ , and is very slightly soluble in alcohol.

Isophthalic and terephthalic acids do not combine with aniline.

T. M. L.

**Derivatives of Diphenylmethane.** By RICHARD E. MEYER and ALFRED CONZETTI (*Ber.*, 1899, 32, 2103—2108).—2:4:2':4'-Tetrahydroxybenzophenone (*Abstr.*, 1897, i, 380) crystallises from water in yellow, glistening needles containing  $1\frac{1}{2}\text{H}_2\text{O}$ , and is readily soluble in methylic or ethylic alcohol, ether, acetone, or acetic acid in the cold, and in water, chloroform, benzene, or toluene on warming; it also dissolves in alkalis and alkali carbonates, yielding non-fluorescent solutions. Although 3:6-dihydroxyxanthone is formed when this compound is heated above its melting point, a better yield may be obtained by Graebe's method (*Abstr.*, 1891, 706); it dissolves readily in alcohol, acetic acid, or acetone, but is practically insoluble in water, benzene, or toluene; its solution in concentrated sulphuric acid has a yellow colour and pale blue fluorescence. Its reduction product (compare Kostanecki and Bistrzycki, *Abstr.*, 1885, 1077) appears to be identical with Möhlau and Koch's formaldehydehydroxyfluorone (*Abstr.*, 1895, i, 46). Its diacetyl derivative,  $\text{C}_{13}\text{H}_6\text{O}_2(\text{OAc})_2$ , crystallises from alcohol in colourless, glistening needles melting at  $200$ — $202^{\circ}$ , and is insoluble in water or alkalis. Tetrabromo-3:6-dihydroxyxanthone,  $\text{C}_{13}\text{H}_2\text{Br}_4\text{O}_2(\text{OH})_2$ , obtained by gently warming acetic acid solutions of bromine and of dihydroxyxanthone, crystallises in colourless needles melting and decomposing at  $280$ — $290^{\circ}$ ; it is insoluble in benzene or toluene, but dissolves fairly readily in hot alcohol or acetic acid; it also dissolves in alkalis, the solutions being colourless, but exhibiting a pale, bluish-violet fluorescence.

Attempts to prepare 3:6-dihydroxyxanthone or its derivatives synthetically on the large scale have proved fruitless. The chief product

obtained by condensing  $\beta$ -resorcylic acid with resorcinol in the presence of acetic anhydride is 1:6-dihydroxyxanthone. The dibromoresorcinol obtained by the elimination of carbonic anhydride from dibromo- $\beta$ -resorcylic acid (Zehenter, Abstr., 1882, 193) is identical with that obtained by fusing eosin with alkali (Baeyer, Abstr., 1877, i, 195), the melting point of both being  $91.5-92.5^\circ$ .

Tetrahydroxydinaphthylmethane (methylenedinaphtharesorcinol) has been prepared by Kahl's method; it yields a *tetracetyl* derivative which crystallises in colourless needles, melts at  $205-206^\circ$ , and is only sparingly soluble in most solvents with the exception of acetone.

J. J. S.

**Derivatives of Fluoran.** By RICHARD E. MEYER and LEO FRIEDLAND (*Ber.*, 1899, 32, 2108—2112. Compare Abstr., 1898, i, 380).—*Nitrofluoran*,  $C_{20}H_{11}O_3 \cdot NO_2$ , obtained by boiling an acetic acid solution of fluoran with nitric acid of sp. gr. 1.5 for an hour, crystallises in rhombic plates melting at  $200-202^\circ$ , and dissolves in concentrated sulphuric acid, giving a yellow, non-fluorescent solution, but is not soluble in cold alcoholic potash. When reduced with stannous chloride and hydrochloric acid, it yields *amidofluoran*, which crystallises from alcohol in colourless plates melting at  $225-228^\circ$ ; it dissolves in cold concentrated sulphuric acid, yielding a yellow solution with a pale green fluorescence, and when warmed turns deep red. When diazotised and boiled with water, it yields fluoran and not hydroxyfluoran.

When fluoran is warmed for some 8 minutes on the water-bath with 10 times its weight of nitric acid of sp. gr. 1.5, and the solution allowed to cool, crystals of 2:7-dinitrofluoran separate, and on pouring into water, a flocculent precipitate of *i-dinitrofluoran* is obtained; this crystallises from acetic acid in thick needles melting at  $217-220^\circ$ , and is insoluble in cold alcoholic potash. When reduced with stannous chloride, it yields *i-diamidofluoran*, which crystallises from alcohol in small, rhombic, strongly doubly refractive crystals melting at  $237-240^\circ$ .

2:7-Dinitrohydroxyfluoranic acid,  $COOH \cdot C_6H_4 \cdot CH < \begin{matrix} C_6H_3(NO_2) \\ C_6H_3(NO_2) \end{matrix} > O$ ,

formed when 2:7-dinitrofluoran is warmed with alcoholic ammonium sulphide, crystallises from acetic acid in large, yellow, flat needles, melting and decomposing at  $245-247^\circ$ ; it is much more readily soluble in alcohol than 2:7-dinitrofluoran, and has acid properties. Its solution in cold alcoholic potash is colourless, but turns red when warmed, or on the addition of water.

J. J. S.

**Meldola and Hughes' Bromindone Derivatives.** By CARL LIEBERMANN and S. SCHLOSSBERG (*Ber.*, 1899, 32, 2095—2102. Compare this vol., i, 372).—The authors have come to the conclusion that the compound described by Meldola and Hughes (*Trans.*, 1890, 396) as bromindone is really  $\beta$ -brom- $\alpha$ -naphthaquinone, and is identical with the compound prepared by Zincke and Schmidt (*Abstr.*, 1895, i, 56) from naphthaquinone dibromide. The bromine atom in bromonaphthaquinone is not readily replaced by aromatic amine residues, and in dibromonaphthaquinone only one of the bromine atoms is readily replaceable by similar residues. Meldola and Hughes' bromindone-

anilide proves to be identical with 2-brom- $\alpha$ -naphthaquinone-3-anilide (compare Miller, Abstr., 1885, 667); it melts at 194°, not at 190°. Their bromohydroxyindone is identical with Merz and Diehl's 2-bromo-3-hydroxynaphthaquinone (Abstr., 1878, 736), the melting point of which is 196—197°, and not 191—192°, and the barium derivative has the composition  $(C_{10}H_4BrO_3)_2Ba + 4H_2O$ . Their bromindone- $\beta$ -naphthylamide appears to be 2-brom- $\alpha$ -naphthaquinone-3-naphthylamide, which may be obtained from dibrom- $\alpha$ -naphthaquinone; the melting point of the pure compound is about 128°, and not 151° (?).

$\alpha$ -Naphthaquinonebenzylamide,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{NH} \cdot \text{CH}_2\text{Ph} \\ \parallel \\ \text{CO} \cdot \text{CH} \end{smallmatrix}$ , obtained from brom- $\alpha$ -naphthaquinone, crystallises in glistening, orange-red needles melting at 156°.

3-Brom- $\alpha$ -naphthaquinone-2-benzylamide,  $CH_2Ph \cdot NH \cdot C \begin{smallmatrix} \text{CBr} \cdot \text{CO} \\ \parallel \\ \text{CO} - C_6H_4 \end{smallmatrix}$ , crystallises in orange-red prisms melting at 109°. J. J. S.

Isonaphthazarine, Tetrahydroxynaphthalene, and Tetraketohydronaphthalene. By THEODOR ZINCKE and A. OSSENBECK (*Annalen*, 1899, 307, 1—28. Compare Abstr., 1892, 720).—Isonaphthazarine (dihydroxynaphthaquinone),  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{OH} \\ \parallel \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$ , prepared from  $\beta$ -naphthaquinone, bleaching powder, and hydrochloric acid, crystallises from glacial acetic acid in brown leaflets with metallic lustre, and from toluene in slender, red needles; it melts at 280° and sublimes when heated strongly. The solution in caustic alkalis is deep blue, becoming colourless when exposed to air, forming phenylglyoxylcarboxylic acid; the barium derivative is reddish-violet and sparingly soluble. The *acetyl* derivative crystallises from glacial acetic acid in orange needles and melts at 172°; the *diacetyl* derivative separates from benzene in slender, white needles, and melts at 105°.

Tetrahydroxynaphthalene,  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \cdot \text{C} \cdot \text{OH} \\ \parallel \\ \text{C(OH)} \cdot \text{C} \cdot \text{OH} \end{smallmatrix}$ , obtained by reducing isonaphthazarine with zinc and sulphuric acid, crystallises from an ethereal solution on adding light petroleum, forming white, silvery leaflets; it gradually decomposes when heated, yielding isonaphthazarine, and is very sensitive towards solvents. The *tetracetyl* derivative crystallises in white needles, and melts at 220°. When tetrahydroxynaphthalene is treated with zinc dust and dilute mineral acids, 1:2:3-trihydroxynaphthalene (naphthapyrogallol) is produced (compare Zincke and Noack, Abstr., 1897, i, 355).

Tetraketohydronaphthalene,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{CO} \\ \parallel \\ \text{CO} \cdot \text{CO} \end{smallmatrix} \cdot 2H_2O$ , prepared by oxidising isonaphthazarine with nitric acid of sp. gr. 1.2, crystallises from nitric acid in large, colourless, monoclinic prisms; it is readily soluble in common media, excepting benzene and light petroleum, but the solutions gradually change, yielding isonaphthazarine, which is also formed when the tetraketone is heated at about 135°. The substance dissolves in alkalis and alkali carbonates, forming colourless solutions which rapidly become blue, and, when acidified, yield isonaphthazarine,

which is also obtained by the action of phenylhydrazine on the tetraketone; aniline and orthophenylenediamine give rise to  $\beta\beta$ -anilido-hydroxy- $\alpha$ -naphthaquinone and naphthadiphenazine (Zincke and Wiegand, Abstr., 1895, i, 616). The *dioxime* of tetraketohydro-naphthalene forms lustrous, greyish leaflets, and melts at  $228^\circ$ ; the *acetyl* derivative crystallises in colourless needles, and melts at  $160^\circ$ ,

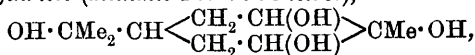
when it decomposes. *Diketonaphthafurazan*,  $C_6H_4 \begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{N} \\ \text{CO}\cdot\text{C}\cdot\text{N} \end{smallmatrix} \text{O}$ , produced when the dioxime is heated with acetic anhydride and sodium acetate, crystallises in long, yellowish needles, and melts at  $198^\circ$ .

$\beta\beta$ -Dinitroso- $\alpha$ -naphthaquinone,  $C_6H_4 \begin{smallmatrix} \text{CO}\cdot\text{C}\cdot\text{NO} \\ \text{CO}\cdot\text{C}\cdot\text{NO} \end{smallmatrix}$ , is formed from the dioxime on oxidation with nitric acid, and crystallises from boiling glacial acetic acid in lustrous, yellow leaflets melting at  $251^\circ$ . The *acid*  $C_{10}H_6N_2O_5$ , obtained by the action of hot, aqueous sodium carbonate on the dinitroso-derivative, melts at  $187^\circ$ , yielding phthalic anhydride; the *silver* salt is crystalline, and the *methylic* salt forms colourless plates melting at  $155^\circ$ . When this acid is reduced with stannous chloride, the *acid*  $C_{10}H_8O_5$  is produced; it crystallises in colourless leaflets on adding benzene to the solution in acetone, and melts at  $145^\circ$ .  
M. O. F.

**Constitution of Pinene.** By GEORG WAGNER and KAZIMIR SLAWINSKI (*Ber.*, 1899, 32, 2064—2083. Compare Abstr., 1894, i, 610; 1896, i, 380).—French turpentine oil, boiling at  $155$ — $156^\circ$ , and having a specific rotatory power  $[\alpha]_D - 37^\circ 30'$ , has been treated with hypochlorous acid according to a slightly modified method, which is described in detail in the original, and the following compounds have been isolated after treating the mixture with potassium hydroxide: Pinole oxide, *sobrerithritol*, a chlorhydrin melting at  $131$ — $132^\circ$ , a second chlorhydrin (B), *nopinolglycol*, and unsaturated compounds.

*cis*-Pinole oxide is identical with that obtained by Wallach (Abstr., 1896, i, 571), and by Wagner and Ginzberg (this vol., i, 618) from pinol; when hydrated, it yields the same glycol as Wallach (Abstr., 1891, 218; 1892, 998) obtained from pinol bromide, and to the oxide and its product of hydration *cis*-configurations are ascribed, whereas the isomeric glycol obtained by oxidising pinol with dilute permanganate is regarded as a *trans*-derivative.

*cis*-Sobrerithritol (*methane*-1 : 2 : 6 : 8-*tetrol*),



melts at  $193$ — $194^\circ$ , is sparingly soluble in ether, but dissolves readily in alcohol or water; it is optically inactive, yields acetic and terpenylic acids on oxidation, and is stereoisomeric with the *sobrerithritol* obtained by the oxidation of inactive *sobrerol* (Abstr., 1896, i, 446). The chlorhydrin obtained from *l*-pinene melts at  $131$ — $132^\circ$ , and is dextrogyrate, having a specific rotatory power  $[\alpha]_D + 88^\circ 23'$ ; *d*-pinene yields a chlorhydrin melting at the same temperature, but having the specific rotatory power  $-87^\circ 39'$ ; the racemate of these two is the chlorhydrin of low melting point previously mentioned (Abstr., 1896, i, 380). The chlorhydrin melting at  $131$ — $132^\circ$ , to which the



constitution  $\text{CHCl} \begin{cases} \text{CMe(OH)} \text{---} \text{CH} \cdot \text{O} \\ \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{CH} \cdot \text{CMe}_2 \end{cases}$  is given, is not readily

acted on by aqueous alkali. When treated with zinc dust and alcohol for several weeks, it yields pinol as the only product; this pinol, when oxidised with permanganate, yields an optically active glycol which the authors term *d-cistrans-pinolglycol*; it melts at  $73\text{--}74.5^\circ$ , is readily soluble in ether or ethylic acetate, and is dextrorotatory; its constitution follows from its products of oxidation, namely, acetic, terpenylic, and terebic acids; the pinol from which it is derived must be the optically active form of ordinary pinol, although it combines with bromine to give ordinary pinol dibromide melting at  $94^\circ$ .

*cis-Menthane-1 : 2-dichlor-6 : 8-diol*, crystallises from boiling ether in small, indefinite crystals melting at  $136\text{--}137^\circ$ ; when warmed with aqueous potassium hydroxide, it readily loses its chlorine atoms and yields *cis*-pinol oxide; it is also attacked in the cold by alkalis, but under these circumstances, in addition to pinol oxide, a small amount of a crystalline chlorhydrin is obtained, which is probably identical with the second chlorhydrin (B) formed in minute quantity by the action of hypochlorous acid on pinene. When treated with alcohol and zinc dust, the dichlorhydrin yields *i*-sobrerol and probably limonene.

*Nopinolglycol*,  $\text{OH} \cdot \text{C}(\text{CH}_2 \cdot \text{OH}) \begin{cases} \text{CH} \cdot \text{O} \\ \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{CH} \cdot \text{CMe}_2 \end{cases}$ , is a derivative of

an isomeride of pinene; it crystallises from ether in prisms melting at  $126\text{--}127^\circ$ , is soluble in water, and, when oxidised, yields formic and a non-volatile, syrupy acid, but no acetic acid; its *acetate* differs from those of the two isomeric pinols in being an oil.

In conclusion, the authors reply to Tiemann's criticisms on their pinene formula. J. J. S.

**Crystallography of a Reduction Product of  $\Delta^4$ -Terpene-3-one.** By WILLIAM H. HOBBS (*Pharm. Arch.*, 1899, 2, 21—23).—The substance, of which only one crystal admitted of examination, was prepared by Kremers (*Abstr.*, 1897, i, 84), being found in the oily reduction product of  $\Delta^4$ -terpene-3-one which had been kept for a year; it is probably a pinacone. The crystal is a light green, orthorhombic plate [ $a : b : c = 0.8857 : 1 : 0.5079$ ]. T. H. P.

**The So-called "Inversion" of Linalool.** By EUGÈNE CHARABOT (*Bull. Soc. Chim.*, 1899, [iii], 21, 549—552. Compare this vol., i, 68).—Attempts were made to obtain an isomeride of linalool by treatment with alcoholic potash. It was found, however, that linalool was unaltered by this reagent. R. H. P.

**Nature of the Isomerism of the Two Lemonals (Citrals).** By LOUIS BOUVEAULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 423—427).—The author discusses his own and Tiemann's investigations on the relation between the two citrals, and concludes that, although it has not been proved that they are not stereoisomerides, it is yet very probable that the isomerism is of a purely chemical nature, and is due to the displacement of a double linking. T. H. P.

**Action of Acids on Citral.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 408—413. Compare Abstr., 1898, i, 557).—*Methylisopropenecyclohexenol*,  $\text{CMe}_2\text{:C} \begin{array}{c} \text{CH}_2 \text{---} \text{CH}_2 \\ \text{CH(OH)---CH} \end{array} \text{CMe}$ , formed on mixing citral with ethylic acetate and 50 per cent. sulphuric acid, boils at  $96\text{--}97^\circ$  under 12 mm. pressure and has a sp. gr. 0.94612. Its index of refraction for the D line at  $16^\circ$  is 1.397, which gives for the molecular refraction (Lorenz and Lorentz formula) the value 46.99; the number calculated from the specific refractions of the constituent atoms is 46.58. It has an agreeable, penetrating odour, recalling orange and bergamot, and quite distinct from that of citral. Its alcoholic nature is shown by its action on sodium, which it dissolves with the liberation of hydrogen and the formation of a sodium derivative. The action of dehydrating agents on it gives rise to cymene. It has the normal molecular weight in benzene.

Citral is reduced by zinc in presence of acetic acid and alcohol, yielding the glycol of citral, 2:6:11:15-tetramethyl-2:6:10:14-octodecatetrene-8:9-diol,  $[\text{CH(OH)CH:CMeCH}_2\text{CH}_2\text{CH:CMe}]_2$ , which boils at  $203\text{--}205^\circ$  under 15 mm. pressure, has a sp. gr. 0.934 at  $0^\circ$ , and for the D line at  $14^\circ$  its index of refraction is 1.500; it dissolves sodium, liberating hydrogen, and has the normal molecular weight in benzene.

T. H. P.

**Condensation of Citral with Cyanacetic Acid.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 413—414).—Cyanacetic acid, citral, and pyridine are heated in a reflux apparatus, the gases evolved being passed first through a wash-bottle containing sulphuric acid to absorb the pyridine, and then through potash tubes to collect the carbonic anhydride. The pyridine is added to stop the polymerising action of the excess of cyanacetic acid. The reaction begins at  $95^\circ$ , and a regular evolution of carbonic anhydride occurs between  $100^\circ$  and  $110^\circ$ , and the heating is stopped when the increase in the weight of the potash tubes corresponds approximately with the theoretical quantity of carbonic anhydride. The liquid is then extracted with ether, and the ethereal solution washed first with dilute sulphuric acid to remove the pyridine, and then with soda solution; after distilling off the ether and fractionating the residue, the greater part of the liquid passes over at  $152\text{--}155^\circ$  under 25 mm. pressure, there being no definite boiling point, owing to polymerisation taking place at each distillation. *Citrylideneacetonitrile*,  $\text{C}_{12}\text{H}_{17}\text{N}$ , so obtained has a peculiar odour, recalling that of pseudoionone, and when treated with dilute acids, yields no cyclic derivative corresponding to ionone; concentrated acids cause it to resinify, even in the cold.

T. H. P.

**Condensation of Citral with Malonic Acid.** By ALBERT VERLEY (*Bull. Soc. Chim.*, 1899, [iii], 21, 414—418).—Molecular proportions of citral, pyridine, and malonic acid, when heated together, give rise to citrylideneacetic acid and *citrylidene malonic acid*,  $\text{CMe}_2\text{:CHCH}_2\text{CH}_2\text{CMe:CHCH:C(COOH)}_2$ ; the latter crystallises from water or alcohol in small, distorted, white prisms melting at  $191^\circ$ . It is insoluble in ether or light petroleum, but is fairly soluble in hot water or alcohol, is very stable towards sulphuric acid or concentrated

potash solution, and loses carbonic anhydride at a temperature above its melting point, yielding citrylideneacetic acid. On treating essence of lemon grass with pyridine and malonic acid, the acid product insoluble in ether contains, in addition to the acid melting at  $191^{\circ}$ , a smaller amount of an acid,  $C_{15}H_{24}O_4$ , melting at  $122^{\circ}$ , which is soluble in water or alcohol, fairly so in ether, but insoluble in light petroleum; it corresponds with an aldehyde homologous with citronellaldehyde, but no such aldehyde could be separated from essence of lemon grass.

*Ethyl citrylideneacetate,*



prepared by heating together ethyl hydrogen malonate, citral, and pyridine in molecular proportion, boils at  $160$ — $162^{\circ}$  under 24 mm. pressure, and has an odour resembling that of pseudoionone.

Citral readily condenses with acetoacetic acid, giving rise to pseudoionone. T. H. P.

**A Polymeride of Citral.** By HENRI LABBÉ (*Bull. Soc. Chim.*, 1899, [iii], 21, 407—408).—On adding, drop by drop, about 100 c.c. of a 1 per cent. alcoholic potash solution to 10 grams of citral, a rise of temperature of  $7^{\circ}$  or  $8^{\circ}$  takes place, the original smell of the citral at the same time disappearing and giving way to a slight, although characteristic, odour. When the liquid is diluted with water and extracted with ether, a quantitative yield of a brownish-yellow oil is obtained. This oil does not crystallise, but it is precipitated from a benzene solution by the addition of light petroleum, in the form of an odourless, yellowish-white powder. When thus purified, it softens at  $75^{\circ}$  and melts between  $81^{\circ}$  and  $82^{\circ}$ ; its empirical formula is  $C_{10}H_{16}O$ , the same as that of citral, of which it is a polymeride. From this, it is concluded that condensation of citral with other products cannot be carried out in dilute alcoholic solution of alkali.

T. H. P.

**Lemonal from the Essential Oil of Lippia Citriodora.** By PHILIPPE BARBIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 635—638).—The essential oil of *Lippia citriodora*, when fractionally distilled, yields 65 to 70 per cent. of a liquid of the composition  $C_{10}H_{16}O$ , which boils at  $106$ — $108^{\circ}$  under 10 mm. pressure, is inactive to polarised light, and has an agreeable odour resembling that of lemons. On oxidation, and on boiling with potassium carbonate solution, this liquid yields the same products as lemonal. With hydroxylamine, it gives two oximes, the one constituting the major portion of the product, boiling at  $119$ — $120^{\circ}$  under 10 mm. pressure, and the other, which is only obtained in small quantity, being identical with lemonaldoxime boiling at  $143$ — $145^{\circ}$  under 10 mm. pressure. By the action of sodium hydrogen sulphite, a compound is obtained which, when decomposed with caustic soda, gives an aldehyde convertible into lemonaldoxime boiling at  $143$ — $145^{\circ}$  under 10 mm. pressure. The oxime from *Lippia citriodora* can also be converted directly into lemonaldoxime by treating its ethereal solution with hydrogen chloride. The oxime boiling at  $119$ — $120^{\circ}$  dissolves in acetic anhydride without evolution of heat, but only yields a small quantity of the nitrile of citric acid, whilst lemonaldoxime gives, with acetic anhydride, a large evolution

of heat and a good yield of the nitrile. Also the aldehyde from the *Lippia* essence gives a mixture of semicarbazides, consisting mainly of the modification melting at  $171^{\circ}$ , whilst lemonal yields principally the form melting at  $135^{\circ}$ .

From these experiments and those of Bouveault (this vol., i, 767), the author concludes that two isomeric lemonals certainly exist, and he is of opinion that they are stereoisomerides. T. H. P.

**Composition of Monarda Oils.** By EDWARD KREMERS and W. E. HENDRICKS (*Pharm. Arch.*, 1899, 2, 73—78).—The oil distilled from *Monarda punctata*, L., contains about 60 per cent. of phenols, consisting mainly of thymol, a little carvacrol sometimes being present. About 10 per cent. of the remainder is an alcoholic compound, the rest, which boils at  $170$ — $180^{\circ}$ , consisting of cymene and a small quantity of dextrorotatory limonene.

*Monarda fistulosa*, L., yields an oil containing cymene, carvacrol, and limonene; if thymol is present, its amount must be less than 2 per cent. of that of the carvacrol. T. H. P.

**Combination of Camphor with Aldehydes.** By ALBIN HALLER (*Compt. rend.*, 1899, 128, 1270—1274).—The author has previously shown (Abstr., 1891, 1498) that crystalline compounds are formed by the interaction of sodiocamphor with various aldehydes of the benzene series. Since the sodiocamphor is mixed with sodioborneol, campholic salts of the acids corresponding with the aldehydes employed are amongst the products. In the case of piperonaldehyde, for example, piperonylic alcohol and piperonylic piperonylate are formed.

The action of meta- or para-methoxybenzaldehyde on sodiocamphor yields a *methoxybenzylidenecamphor*,  $C_8H_{14} \begin{smallmatrix} \text{C}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ | \\ \text{CO} \end{smallmatrix}$ . The

meta-derivative forms long, white needles which melt at  $51$ — $52^{\circ}$  and are much more soluble in organic solvents than the ortho- or para-compounds, the para-derivative forms rhombic crystals with an angle  $114\cdot45^{\circ}$ , and melts at  $125^{\circ}$ . When treated with sodium amalgam in presence of alcohol, each is reduced to a *methoxybenzyl-*

*camphor*,  $C_8H_{14} \begin{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \\ | \\ \text{CO} \end{smallmatrix}$ ; the meta-derivative is an oily

liquid which boils at  $205$ — $206^{\circ}$  under 10 mm. pressure, and the para-derivative forms rhombic prisms with an angle of  $105\cdot45^{\circ}$  which melt at  $71^{\circ}$ . It is noteworthy that in the two sets of compounds the meta-derivative has the lowest and the para-derivative the highest melting point.

*Piperonylidenecamphor*,  $C_8H_{14} \begin{smallmatrix} \text{C}:\text{CH}\cdot\text{C}_6\text{H}_3\cdot\text{O}_2\cdot\text{CH}_2 \\ | \\ \text{CO} \end{smallmatrix}$ , obtained in a similar manner, forms colourless needles which melt at  $159\cdot5^{\circ}$ . When reduced, it yields the corresponding piperonylcamphor which crystallises in small, white lamellæ melting at  $70^{\circ}$ .

Piperonylic piperonylate crystallises in needles, melts at  $97^{\circ}$  and is hydrolysed by alcoholic potash; cryoscopic measurements show that its molecular weight is 300. Piperonylic alcohol crystallises in white, flattened needles which melt at  $51$ — $52^{\circ}$ .

All the aldehydic derivatives of camphor are characterised by the ease with which they are reduced to alkylic camphors, the reduction affecting first the group C:C and afterwards the CO group.

C. H. B.

**Corrosion Figures showing the Enantiomorphous Structure of Benzylidenecamphors.** By JULES MINGUIN (*Compt. rend.*, 1899, 128, 1335—1336).—When optically active benzylidenecamphor is immersed for about a minute in benzene, the crystals show, on the faces *m*, corrosion figures which are distinctly unsymmetrical, the figures being generally directed from the angle *a* to the angle *e* of the prism. The figures formed on the dextrogyrate compound are enantiomorphous with those formed on the lævograte compound. No precise results have as yet been obtained with faces other than *m*.

C. H. B.

**Desmotropic Forms of Camphor Methylenephnylhydrazone.** By MARIO BETTI (*Ber.*, 1899, 32, 1995—1999).—The product of the action of diazobenzene chloride on sodium camphorcarboxylate melts at 165°, but when recrystallised from alcohol, it separates in stout, brownish-yellow needles and melts at 180°; the melting point is unchanged by crystallising from benzene. When dissolved in cold benzene, the substance gives a deep ruby-red coloration with ethereal ferric chloride and is therefore regarded as the *enolic form* of camphor

*methylene- or α-phenylhydrazone*,  $C_8H_{14} \begin{smallmatrix} & C:N:N \cdot Ph \\ & | \\ C & \cdot OH \end{smallmatrix}$ .

When a trace of piperidine is added to a solution of the substance in benzene, small, yellow crystals are deposited which melt at 155° and give no immediate coloration with ferric chloride, although the characteristic red coloration of the enolic form appears after some hours. The form melting at 155° is regarded as the *ketonic* modification,

$C_8H_{14} \begin{smallmatrix} & C:N \cdot NHPh \\ & | \\ C & \cdot O \end{smallmatrix}$

The ketonic, like the enolic, form can be crystallised unchanged from benzene, but on crystallising twice from 95 per cent. alcohol the enolic form melting at 180° is deposited.

A mixture of the two forms, melting at 167°, is produced on crystallising the enolic form from glacial acetic acid; a similar mixture is produced on precipitating a cold alcoholic solution of the enolic form with dilute potash, but water alone precipitates the enolic form. A mixture melting at 165° is produced by heating either the enolic or the ketonic form at the melting point for some time, and then crystallising from benzene, and also by crystallising the ketonic form repeatedly from benzene.

T. M. L.

**Action of Certain Gases on Caoutchouc.** By A. D'ARSONVAL (*Compt. rend.*, 1899, 128, 1545—1546).—When caoutchouc is left for a time in carbonic anhydride at pressures of from 1 to 50 atmospheres, it absorbs large quantities of the gas and swells considerably, in some cases having expanded to as much as 10 or 12 times the original volume. After this treatment, the caoutchouc is more gelatinous and less elastic than before, and, on leaving it in the air,

bubbles of carbonic anhydride are given off with a faint noise. Carbonic anhydride at ordinary pressure readily passes through a caoutchouc bag, the rate of deflation increasing with the pressure of the gas. With oxygen, the escape is less rapid, and still less so with nitrogen, this last being hence recommended for the inflation of pneumatic tyres. T. H. P.

**Cerin and Friedelin.** By CONSTANTIN I. ISTRATI and ADRIANO OSTROGOVICH (*Compt. rend.*, 1899, 128, 1581—1584).—By extracting cork with chloroform and fractionally crystallising the extract, cerin and friedelin were obtained.

Cerin is a white, silky substance melting at  $234-234.5^{\circ}$  (corr.), and is slightly soluble in ethylic alcohol, acetate, or ether, but more so in chloroform, benzene, ethylenic bromide, nitrobenzene, or phenol. It has the composition  $C_{27}H_{44}O_2$ , which agrees with the molecular weight determined by the boiling point method (the compositions previously assigned to it were: Döpping,  $C_{25}H_{20}O_3$ ; Siewert,  $C_{17}H_{28}O$ ; Kügler,  $C_{20}H_{32}O$ ; and Thoms,  $C_{30}H_{50}O_2$ , or  $C_{35}H_{54}O_2$ ). The specific rotatory power in chloroform solution varies with the concentration, having at  $24^{\circ}$  its maximum value  $-84.69^{\circ}$  for a saturated 0.3306 per cent. solution; a supersaturated 0.431 per cent. solution gives a specific rotation  $-81.20^{\circ}$ .

**Friedelin**,  $C_{43}H_{70}O_2$ , which is the fraction more soluble in chloroform, crystallises from alcohol in long, flat, brilliant needles melting at  $263-263.5^{\circ}$  (corr.). It is soluble in the same solvents as cerin, but to a greater extent, and in chloroform solution has the normal molecular weight. The specific rotation in chloroform at  $24^{\circ}$  has its maximum value  $-48.72^{\circ}$  for a 0.821 per cent. solution.

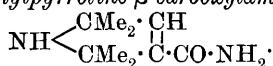
Of the two reactions given by Thoms (this vol., ii, 324) for his cerin, one is given by both cerin and friedelin, namely, the formation of a rose-red coloration on the addition of concentrated sulphuric acid to an acetic anhydride solution of the substance; but neither of the authors' compounds gives with a mixture of chloroform and sulphuric acid a yellow colour changing to violet. T. H. P.

**Study of Ivy: Preparation of Hederin.** By HOUDAS (*Compt. rend.*, 1899, 128, 1463—1465).—The author has separated from ivy a glucoside, *hederin*,  $C_{64}H_{104}O_{10}$ , which crystallises from alcohol in long, radiating groups of thin needles, and melts at  $248^{\circ}$  to a slightly amber-coloured liquid; a determination of the molecular weight by the ebullioscopic method agreed with the formula given. Hederin has an almost imperceptible, sweetish flavour, and in alcoholic solution at  $22^{\circ}$  has  $[\alpha]_D + 16.27^{\circ}$ . It is insoluble in water, light petroleum, or chloroform, but dissolves slightly in ether or benzene, and more so in alcohol or acetone. It is readily dissolved by hot alkaline hydroxides or carbonates. When boiled for 12 hours with 4 per cent. sulphuric acid in a reflux apparatus, hederin gives rise to an insoluble product, hederidin, and to two sugars, hederose and rhamnose.

**Hederidin**,  $C_{26}H_{40}O_4$ , crystallises from boiling alcohol in sparkling rhomboidal prisms which are insoluble in water, ether, benzene, or chloroform; these melt at  $324^{\circ}$  and sublime undecomposed.

*Hederose*,  $C_6H_{12}O_6$ , crystallises in shining, concentrically grouped needles, and is very soluble in water or boiling alcohol. It melts at  $155^\circ$ , and in solution exhibits birotation; the boiled solution at  $22^\circ$  gives  $[\alpha]_D + 102.66$ .  
T. H. P.

**Formation of Pyrroline and Pyrrolidine Derivatives from Triacetonamine.** I. By HERMANN PAULY and JOSEPH ROSSBACH (*Ber.*, 1899, **32**, 2000—2014. Compare *Abstr.*, 1898, i, 382).—The substance previously described (*loc. cit.*) as ‘iminotriacetonamine’ is shown to be  $\alpha$ -tetramethylpyrroline- $\beta$ -carboxylamide,



It decolorises potassium permanganate in acid solution, does not interact with hydroxylamine, phenylhydrazine, or hydrogen cyanide, and has a normal molecular weight in boiling benzene. The *monacetyl* derivative is precipitated by ether from acetic acid solution in crystalline aggregates and melts at  $256$ — $256.5^\circ$ . The *mononitrosamine* crystallises from acetone in fine, white needles and melts at  $201^\circ$ . The *perbromide*,  $C_9H_{16}ON_2 \cdot HBr \cdot Br_2$ , crystallises from glacial acetic acid in yellowish-red flakes and melts at  $201^\circ$ ; it is very stable in the dry state, but loses bromine when boiled with water or acetone; by prolonged heating at  $120^\circ$ , it loses 1 mol. of bromine and leaves the hydrobromide of the base; the bromine test gives, therefore, no indication of the double bond.

The *hydriodide* of 1-methyl- $\alpha$ -tetramethylpyrroline- $\beta$ -carboxylamide,  $NMe \begin{array}{c} \diagup CMe_2 \cdot CH \\ \diagdown CMe_2 \cdot \dot{C} \cdot CO \cdot NH_2 \end{array} \cdot HI$ , crystallises from a mixture of methylic alcohol and ethylic acetate in fine needles, and dissolves very readily in water and alcohol; it becomes yellowish when dried at  $110^\circ$  and melts at  $221$ — $222^\circ$ . The methylated *base* crystallises from light petroleum in rhombic tablets, dissolves very readily in water, alcohol, ether, acetone, or boiling benzene, and melts at  $104^\circ$ ; when a solution in light petroleum is dried over potash, the *potassium salt* of the base separates as a white powder (compare pyrrole and benzamide), but is decomposed by water. All the salts are very soluble.

*Tetramethylpyrrolinecarboxylmethylamide*,  $NH \begin{array}{c} \diagup CMe_2 \cdot CH \\ \diagdown CMe_2 \cdot \dot{C} \cdot CO \cdot NHMe \end{array}$ , isomeric with the preceding base, is produced by the action of methylamine on dibromotriacetonamine; it separates from ether in silky, thread-like needles which melt at  $66$ — $67^\circ$ , and distils undecomposed in a vacuum, the melting point rising to  $78^\circ$ . The *aurichloride* crystallises in prisms, and when dried over sulphuric acid melts at  $190^\circ$ .

$\alpha$ -Tetramethylpyrrolidine- $\beta$ -carboxylamide,  $NH \begin{array}{c} \diagup CMe_2 \cdot CH_2 \\ \diagdown CMe_2 \cdot \dot{C}H \cdot CO \cdot NH_2 \end{array}$ , produced by reduction of the pyrroline base with sodium amalgam, crystallises from toluene and melts at  $121^\circ$ , but when dried by distillation in a vacuum, melts at  $129$ — $130^\circ$ ; it is slightly soluble in water, benzene, toluene, or ether, but readily in alcohol or acetone. The *hydrochloride* is easily soluble in water, less readily in alcohol. The

*hydrobromide* forms small, glistening, prismatic crystals and melts at 256°. The *picrate* separates from water in yellow, glistening prisms and melts at 189°. The *aurichloride*,  $C_9H_{15}ON_2 \cdot HAuCl_4$ , crystallises from water in large, golden-yellow, flat needles and melts at 210°. The *platinochloride*,  $(C_9H_{15}ON_2)_2 \cdot H_2PtCl_6$ , crystallises from alcohol in orange-yellow, rhombic tablets, and dissolves readily in water, but deposits ammonium platinochloride on boiling the solution. *Nitroso-tetramethylpyrrolidinecarboxylamide* crystallises from water in slender, white needles and melts at 229°.

The *hydriodide* of 1-methyl- $\alpha$ -tetramethylpyrrolidine- $\beta$ -carboxylamide  $NMe \begin{smallmatrix} \diagup CMe_2 \cdot CH_2 \\ \diagdown CMe_2 \cdot CH \cdot CO \cdot NH_2 \end{smallmatrix} HI$ , crystallises from 80 per cent. alcohol in short, glistening prisms and melts at 250°; it dissolves easily in water and less readily in alcohol and wood spirit. The *base* crystallises from acetone in slender needles and melts at 142–144°, but can only be dried completely by distillation in a vacuum; it does not decolorise acid potassium permanganate solution, and is not acted on by nitrous acid. The *picrate* crystallises from alcohol in hair-like needles and melts at 160°. The *aurichloride* crystallises in quadratic tablets and melts at 172°. The *platinochloride* separates in brown, microscopic prisms and melts at 227°.

Tetramethylpyrrolidinecarboxylamide is most readily hydrolysed by aqueous alkalis, but can also be hydrolysed by heating at 130° with concentrated hydrochloric acid. The *hydrochloride* of  $\alpha$ -tetramethylpyrrolidine- $\beta$ -carboxylic acid,  $NH \begin{smallmatrix} \diagup CMe_2 \cdot CH \\ \diagdown CMe_2 \cdot C \cdot COOH \end{smallmatrix} HCl + 2H_2O$ , crystallises from water in well-formed, thick, six-sided tablets. The *aurichloride*,  $C_9H_{15}NO_2 \cdot HAuCl_4 \cdot H_2O$ , crystallises in slender, golden needles, sinters at 150°, and melts at 185°. The *acid* crystallises from hot water as a glistening powder and melts at 300°; it is much more readily soluble in cold water, and on evaporation the solution deposits fine, well-formed, thick, monoclinic prisms, or large six-sided tablets containing  $2H_2O$ . The *methylie* salt boils at 201° under 740 mm. pressure, and forms an insoluble, mobile, colourless fluid, with a faint, stupefying odour; the *ethylie* salt boils at 212° under 740 mm. pressure, and when acted on with ammonia in methylie alcohol, re-forms the original amide.  
T. M. L.

**Derivatives of Picoline.** By ARNOLD HESS (*Ber.*, 1899, 32, 1985–1987).—*Nitroso-4 : 6-dihydroxy-2-picoline*, prepared by the action of nitrous acid on dihydroxypicoline, is a yellow powder readily soluble in water; it dissolves in alkalis to a green solution, is only slightly soluble in hydrochloric and sulphuric acids, and is insoluble in light petroleum; with ferric chloride, it gives a green solution and a dark precipitate; it crystallises from alcohol in glistening, brown scales, but on boiling the solution decomposition occurs, and a dark-coloured substance separates which contains a smaller percentage of nitrogen; on heating, the nitroso-compound explodes without melting. By the action of stannous chloride and hydrochloric acid, the nitroso-compound is not reduced, but is converted into a *trihydroxypicoline*, which crystallises from water in violet needles and melts at 263–265°;



with ferric chloride, it gives an intense blue coloration, which becomes red in alkaline and green in acid solution; the blue colour disappears on heating the solution, but reappears on cooling, the first appearance of colour being on the surface exposed to the oxidising action of the air. The *hydrochloride* forms large, rhombic crystals, which melt at 85—90°, lose water and hydrogen chloride at 100°, and finally melt at 263—265°.

The trihydroxypicoline is isomeric with that described by Sedgwick and Collie (*Trans.*, 1895, 67, 412) which melts at 179°, but is perhaps identical with their compound melting at 252° (corr. 262°).

T. M. L.

**Quinazoline Compounds.** By GOTTFRIED HANSCHKE (*Ber.*, 1899, 32, 2021—2030. Compare Fröhlich, *Abstr.*, 1885, 154).—6-*Amido-3-methylbenzophenone*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CH}_3$ , is readily soluble in ether, alcohol, chloroform, acetone, acetic acid, or light petroleum, crystallises in yellow needles or long, six-sided tablets, sinters at 60°, and melts at 64°. The *hydrochloride* forms white needles which melt and decompose at 179—180°, becomes yellowish-brown in the air, and is decomposed by water. The *picrate* forms yellow prisms and melts at 145°. The *benzoyl* derivative separates from alcohol in cubes or slender needles, and melts at 114—116°.

4'-*Phenyl-3-methyl-2'-ketodihydroquinazoline*,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CPh:N} \\ \text{NH-CO} \end{smallmatrix}$ , produced by heating the base with carbamide, crystallises from alcohol in colourless prisms and melts at 283—285°; it is insoluble in water or ether, slightly soluble in alcohol, readily in acetic acid, and is dissolved by alkalis and acids, the latter giving a yellow solution. The *hydrochloride* forms yellow needles, and is dissociated by heating, and slowly when left in a vacuum over lime. The *nitrate* separates in yellow, glistening needles, and froths up when heated to 200°, leaving a substance which melts at 250°. The *dichromate* crystallises in orange-coloured needles or flakes. The *benzoyl* derivative crystallises from alcohol in flat needles or rhombic tablets, and melts at 121—122°.

2'-*Chloro-4'-phenyl-3-methylquinazoline*,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CPh:N} \\ \text{N}=\text{CCl} \end{smallmatrix}$ , crystallises from alcohol in slender, colourless needles and melts at 140—141°; it dissolves in acids, but is reprecipitated by water.

4'-*Phenyl-3-methyl-3':4'-dihydroquinazoline*,  $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{CHPh:NH} \\ \text{N}=\text{CH} \end{smallmatrix}$ , separates from alcohol in stout, well-formed crystals, and melts at 186—188°; the base, like its salts, is only slightly soluble in water, and has a bitter taste. The *hydrochloride* melts at 240°. The *nitrate* is even less soluble than the hydrochloride; it melts at 186° with vigorous frothing. The *picrate* crystallises from alcohol and melts at 173—175°, but sinters at a lower temperature. The *dichromate* separates as a yellow powder, which becomes brown on the surface when exposed to air. The *ferrocyanide* forms colourless, well-formed crystals. The *benzoyl* derivative crystallises from alcohol in thread-like needles and melts at 185—186°.

6-*Amido-3-methylbenzhydrol*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CHPh} \cdot \text{OH}$ , separates

from dilute alcohol in white, ill-defined crystals, and melts at 82—84°; it dissolves in hydrochloric acid, but does not form a stable salt, and decomposes on boiling the solution, emitting an odour of benzaldehyde.

4'-Phenyl-3-methyl-2'-ketotetrahydroquinazoline,  $C_6H_5Me \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{NH} - \text{CO} \end{smallmatrix}$ ,

produced by heating the benzhydrol with carbamide, crystallises from alcohol in square leaflets and melts at 206—207°. The *acetate*,  $C_{15}H_{14}N_2O_2 \cdot C_2H_4O_2$ , softens at 120° and melts at 190°. The *picrate* crystallises from alcohol in yellow needles and melts at 157—158°.

4'-Phenyl-3-methyl-2'-thiotetrahydroquinazoline,  $C_6H_5Me \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{NH} - \text{CS} \end{smallmatrix}$ ,

prepared by the action of thiocyanic acid on the benzhydrol, separates from hot acetic acid in stout, well-developed crystals, dissolves slightly in alcohol, but not in water, becomes brown at 240°, sinters at 250°, and melts at 265—270° with evolution of gas. By the action of bromine, it is converted into the 4'-phenyl-3-methyl-2'-bromodihydro-

quinazoline hydrobromide,  $C_6H_5Me \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{N} = \text{CBr} \end{smallmatrix} \cdot \text{HBr}$ , which separates from the acetic acid solution in large, well-formed rhombohedra, dissolves readily in alcohol, becomes brown on heating, sinters at 240°, and melts at 255°. The *base* crystallises from alcohol in slender prisms and melts at 155°. By the action of sodium carbonate on the alcoholic solution, the bromine is removed, and 4'-phenyl-3-methyl-2'-ketotetrahydroquinazoline is produced. Reduction with hydriodic acid and phosphorus gives 4'-phenyl-3-methyldihydroquinazoline.

By the condensation of phthalylparatoluidide with benzoic chloride, there is produced, in addition to the phthalyl derivative of 6-amido-3-methylbenzophenone, an isomeric base, which is probably 5-amido-2-methylbenzophenone (?). The base, which was obtained as a yellow oil, gives a *benzoyl* derivative which separates from alcohol in white needles and melts at 136—138°. The *sulphate* melts at 147—149°, dissolves unchanged in cold water, but is partly decomposed on boiling the solution. The *hydrochloride* melts between 120° and 150°.

T. M. L.

### 1-Ethylphthalazine and some Derivatives of Phthalazone.

By VICTOR PAUL (*Ber.*, 1899, 32, 2014—2021. Compare *Abstr.*, 1898, i, 211).—4'-Chlorophthalazine *picrate*,  $C_6H_4 \begin{smallmatrix} \text{CH:N} \\ \text{CCl:N} \end{smallmatrix} \cdot C_6H_5N_3O_7$ , crystallises in long needles and melts at 135°. The *platinochloride*,  $(C_8H_5ClN_2)_2 \cdot H_2PtCl_6$ , separates in orange-yellow needles and melts at 205°. The *ferrocyanide*,  $(C_8H_5N_2Cl)_2 \cdot H_4Fe(CN)_6$ , forms orange-yellow needles which, when heated, decompose without melting.

Phthalazine *hydriodide*,  $C_6H_4 \begin{smallmatrix} \text{CH:N} \\ \text{CH:N} \end{smallmatrix} \cdot HI$ , forms lemon-yellow crystals, dissolves readily in water, becomes brown at 200°, and melts at 203°. The *ferrocyanide*,  $(C_8H_6N_2)_2 \cdot H_4Fe(CN)_6$ , forms yellow prisms and has no melting point. The *aurichloride*,  $C_8H_6N_2 \cdot HAuCl_4$ , forms yellow needles and melts at 200°.

4':1'-Chlorethylphthalazine is obtained from 1'-ethylphthalazone

(m. p. 168—169°) by heating with phosphorus oxychloride (Abstr., 1898, i, 212); it melts at 93°. The *hydrochloride*,  $C_{10}H_9N_2Cl \cdot HCl$ , dissolves very easily in water, crystallises from absolute alcohol in stout needles, and melts at 183—184°. The *aurichloride*,  $C_{10}H_9N_2Cl \cdot HAuCl_4$ , separates in yellow needles, melts at 116°, and decomposes with frothing at 150°. The *platinochloride*,  $(C_{10}H_9N_2Cl)_2 \cdot H_2PtCl_6$ , is golden-yellow. The *ferrocyanide*,  $(C_{10}H_9N_2Cl)_2 \cdot H_4Fe(CN)_6$ , crystallises in orange-coloured needles. The *picrate*,  $C_{10}H_9N_2Cl \cdot C_6H_3N_3O_7$ , separates in yellow needles. The *dichromate*,  $(C_{10}H_9N_2Cl)_2 \cdot H_2Cr_2O_7$ , forms orange-coloured needles which explode without melting.

4' : 1'-Iodoethylphthalazine,  $C_6H_4 \begin{smallmatrix} \text{CEt} \cdot \text{N} \\ \text{CH} = \text{N} \end{smallmatrix}$ , melts at 78°. The *hydriodide*,  $C_{10}H_9N_2I \cdot HI$ , forms feebly-soluble, orange-yellow needles which darken at 175° and melt at 178°. The *hydrochloride* forms yellow needles and melts at 173°; it is somewhat more soluble than the *hydriodide*. The *picrate* separates in long, yellow needles, and melts at 141°. The *platinochloride* forms yellow needles.

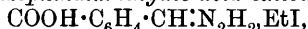
1'-Ethylphthalazine,  $C_6H_4 \begin{smallmatrix} \text{CEt} \cdot \text{N} \\ \text{CH} = \text{N} \end{smallmatrix}$ , distils at 206° under 25 mm. pressure, and at 190° under 16 mm. pressure, but decomposes when distilled under atmospheric pressure; it solidifies in a vacuum to a hard mass melting at 23·5°; the base is miscible with water, does not reduce Fehling's solution, becomes brown in the air, dissolves readily in ordinary solvents, has a neutral reaction, and an odour resembling that of acacia blossoms. The *hydriodide* is precipitated by ether from its alcoholic solution in yellow needles which become brown at 200° and melt at 203°. The *hydrochloride* dissolves readily in water, crystallises from 96 per cent. alcohol in colourless prisms, and melts at 216°. The *picrate* forms golden-yellow needles and melts at 175° with evolution of gas. The *platinochloride* separates in slightly soluble, orange-coloured needles, and melts with frothing at 180°. The *aurichloride* forms golden-yellow needles, melts at 144°, and decomposes at 175°. The *dichromate* forms slightly soluble, orange-coloured needles which explode when heated rapidly. The *ferrocyanide* forms sparingly soluble, yellow needles.

1'-Ethyltetrahydrophthalazine,  $C_6H_4 \begin{smallmatrix} \text{CHEt} \cdot \text{NH} \\ \text{CH}_2 - \text{NH} \end{smallmatrix}$ , is an oil which does not appear to form any insoluble salts. The *hydrochloride* forms colourless crystals, melts at 168°, dissolves very readily in water, and reduces Fehling's solution in the cold. The *dibenzoyl* derivative separates from alcohol in pointed columns and melts at 159°. The *methiodide*,  $C_{10}H_{10}N_2 \cdot MeI$ , separates from benzene solution in long, golden-yellow needles, becomes red at 117°, melts at 129°, and dissolves readily in water. The corresponding *picrate* forms golden-yellow needles and melts at 171°.

By the action of caustic potash, ethylphthalazine methiodide is converted into 3'-methyl-1'-ethyldihydrophthalazine,  $C_6H_4 \begin{smallmatrix} \text{CEt} \cdot \text{N} \\ \text{CH}_2 \cdot \text{NMe} \end{smallmatrix}$ , and 3'-methyl-1'-ethylphthalazone,  $C_6H_4 \begin{smallmatrix} \text{CEt} \cdot \text{N} \\ \text{CO} - \text{NMe} \end{smallmatrix}$ .

The *picrate* of 3-methyl-1-ethyl-dihydrophthalazine crystallises from alcohol in alizarin-red needles and melts at  $108^{\circ}$ ; the *platinochloride* forms long, golden-yellow needles; the *ferrocyanide* forms yellow needles which decompose without melting. 3'-Methyl-1'-ethylphthalazone, unlike the dihydro-base, is not volatile with steam; it forms crystals melting at  $78-79^{\circ}$ , and distils without decomposition.

The ethylation of phthalazone gives 3'-ethylphthalazone and the ethiodide described below. 3'-Ethylphthalazone,  $C_6H_4 \begin{smallmatrix} \text{CH:N} \\ \text{CO}\cdot\text{NEt} \end{smallmatrix}$ , distils at  $295^{\circ}$  and solidifies to a colourless, crystalline mass which melts at  $55^{\circ}$ . Hydrazophthalaldehydic acid ethiodide,



is precipitated in needles on adding ether to a cold, alcoholic solution, becomes yellow, and melts at  $171^{\circ}$ , losing water and ethylic iodide, after which it melts again at  $181^{\circ}$ , the melting point of phthalazone.

T. M. L.

**Camphopyrazolones.** By H. WAHL (*Ber.*, 1899, 32, 1987—1991).

—1-Phenyl-4:5-campho-3-pyrazolone,  $C_8H_{14} \begin{smallmatrix} \text{C}\cdot\text{CO} \\ \text{C}\cdot\text{NPh} \end{smallmatrix} \text{NH}$ , produced by heating together ethylic camphorcarboxylate and phenylhydrazine, crystallises from acetic acid and melts with partial decomposition at  $285^{\circ}$ .

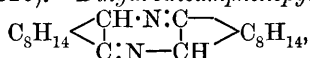
1-Phenyl-4:5-campho-3-benzoyloxy-pyrazole,  $C_8H_{14} \begin{smallmatrix} \text{C}\cdot\text{C(Obz)} \\ \text{C}\cdot\text{NPh} \end{smallmatrix} \text{N}$ , prepared by the action of benzoic chloride and potash on the pyrazolone, crystallises from dilute alcohol in needles and melts at  $111.5^{\circ}$ . The *methiodide* melts and decomposes at  $175^{\circ}$ , and when warmed with dilute sodium hydroxide is converted quantitatively into 1-phenyl-2-methyl-4:5-campho-3-pyrazolone (camphoisoantipyrene),  $C_8H_{14} \begin{smallmatrix} \text{C}\cdot\text{CO} \\ \text{C}\cdot\text{NPh} \end{smallmatrix}$ ; this crystallises from dilute alcohol or from ethylic acetate in well-formed tablets, melts at  $182-183^{\circ}$ , dissolves slightly in hot water, and gives a dark-red coloration with ferric chloride.

1-Phenyl-3:4-campho-5-pyrazolone,  $C_8H_{14} \begin{smallmatrix} \text{C}\cdot\text{NH} \\ \text{C}\cdot\text{CO} \end{smallmatrix} \text{NPh}$ , prepared by the action of phosphorus trichloride on ethylic camphorcarboxylate and phenylhydrazine dissolved in toluene, crystallises from alcohol in minute needles and melts at  $152^{\circ}$ . 1-Phenyl-3:4-campho-5-benzoyloxy-pyrazole,  $C_8H_{14} \begin{smallmatrix} \text{C}\cdot\text{NH} \\ \text{C}\cdot\text{C(Obz)} \end{smallmatrix} \text{NPh}$ , crystallises from dilute alcohol in white flakes and melts at  $121-122^{\circ}$ . The *methiodide* melts and decomposes at  $170^{\circ}$ . 1-Phenyl-2-methyl-3:4-campho-5-pyrazolone (camphoantipyrenin),  $C_8H_{14} \begin{smallmatrix} \text{C}\cdot\text{NMe} \\ \text{C}\cdot\text{CO} \end{smallmatrix} \text{NPh}$ , crystallises from alcohol in white, glistening needles, melts at  $193^{\circ}$ , dissolves slightly in hot water, and gives a brownish-red coloration with ferric chloride.

The methylated campho-3-pyrazolone, like the so-called isoantipyrene, is poisonous, but the 5-pyrazolone has a physiological action like that of antipyrene.

T. M. L.

**Synthetical Bases of the Series of Terpenes and Camphors.**  
By PAUL DUDEN and W. PRITZKOW (*Annalen*, 1899, 307, 207—230.  
Compare this vol., i, 626).—*Dihydrodicamphenepyzazine*,



prepared by heating amidocamphor on the water-bath during 5 hours, is also produced when the primary base is exposed to summer temperatures during several days, and crystallises from ether or petroleum in colourless prisms melting at  $116^\circ$ ; it is not very volatile in steam, and is indifferent towards mercuric oxide, ammoniacal silver solution, and Fehling's solution. Methyl iodide unites with dihydrodicamphenepyzazine, forming a yellow oil, which is resolved at  $200^\circ$  into methyl iodide and dicamphenepyzazine. The *monohydrochloride* crystallises from water in long, flat prisms, melts at  $258^\circ$ , and is acid towards litmus; the *dihydrochloride* melts at  $260^\circ$ , and loses  $\text{HCl}$  in a desiccator. The *nitrate* forms colourless needles, decomposing at  $88^\circ$ , and the *picrate* crystallises from alcohol in lustrous leaflets; the *silver nitrate* compound,  $\text{C}_{20}\text{H}_{30}\text{N}_2 \cdot \text{AgNO}_3$ , crystallises in long, slender needles, containing  $1\text{H}_2\text{O}$ , and decomposes at  $187^\circ$ .

*Dicamphenepyzazine*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{NH} \cdot \text{C} \\ \text{C} \cdot \text{NH} \cdot \text{C} \end{array} \text{C}_8\text{H}_{14}$ , obtained by oxidising dihydrodicamphenepyzazine with ferric chloride, crystallises from alcohol in long needles and melts at  $157^\circ$ , boiling at  $326^\circ$  under 748 mm. pressure; reduction with tin and hydrochloric acid regenerates the dihydro-derivative. The *hydrochloride* is a crystalline powder, the *platinochloride* forms orange prisms, and the *aurichloride* decomposes at  $240^\circ$ ; the *mercurichloride* crystallises from dilute alcohol in colourless needles and decomposes at  $249^\circ$ . The *silver nitrate* compound crystallises in thin, four-sided plates, and melts above  $270^\circ$ . The *methiodide* crystallises from water in concentric aggregates of long needles containing  $1\text{H}_2\text{O}$ ; the *platinochloride* of the ammonium base crystallises from dilute hydrochloric acid in small prisms and decomposes above  $260^\circ$ .

*Dicamphanepyzazine*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH} \cdot \text{NH} \cdot \text{CH} \\ \text{CH} \cdot \text{NH} \cdot \text{CH} \end{array} \text{C}_8\text{H}_{14}$ , prepared by reducing the foregoing pyrazine bases in alcoholic solution with sodium, melts at  $147^\circ$ ; the *hydrochloride* crystallises from alcohol in slender needles, remaining unfused at  $275^\circ$ , and the *nitrate* crystallises in long needles, and melts, evolving gas, at  $180^\circ$ . The *sulphate* forms prisms; the *picrate* crystallises from water in thin, lustrous leaflets, and decomposes at  $235^\circ$ ; the *dinitrosamine* separates from alcohol in thin, six-sided plates melting at  $215^\circ$ . M. O. F.

**Coloured Salts of Violuric Acid and other Oximidoketones.**  
By J. GUINCHARD (*Ber.*, 1899, 32, 1723—1741).—Oximidomethylisoxazolone,  $\text{NOH} \cdot \text{C} \begin{array}{c} \text{CO} \cdot \text{O} \\ \text{CMe} \end{array} \text{N}$ , is a colourless substance, but gives a red solution with alkalis which is decolorised when the alkali is in excess owing to the formation of a colourless salt of methylglyoxime-carboxylic acid,  $\text{NOH} \cdot \text{CMe} \cdot \text{C}(\text{NOH}) \cdot \text{COOH}$ . The *potassium* salt, to

which the formula  $\begin{array}{c} \text{O} \cdot \text{C}(\text{OK}) \cdot \text{O} \\ | \\ \text{N} : \text{C} \cdot \text{CMe} : \text{N} \end{array}$  is assigned, separates from alcohol as a rosy-red powder which slowly decomposes with evolution of hydrogen cyanide; with water it gives a red solution which slowly loses its colour, the solutions in ethylic and methylic alcohols are more stable. The *acid potassium* salt,  $\text{C}_4\text{H}_3\text{N}_2\text{O}_3\text{K} + \text{C}_4\text{H}_4\text{N}_2\text{O}_3$ , is yellow, but is split up into its components by water and gives a red solution. It also yields a yellow *acid* and a red *normal ammonium* salt. The *silver* salt, when treated with methylic iodide, gives a colourless *methylic* salt,  $\text{NOMe} : \text{C} \begin{array}{c} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CMe} \end{array} \text{N}$ , which crystallises from light petroleum and melts at  $65-66^\circ$ ; it is only slightly soluble in water or light petroleum, but readily in alcohol and ether; it slowly dissolves in alkalis, giving a colourless solution of a salt of the acid  $\text{NOH} : \text{CMe} : \text{C}(\text{NOMe}) : \text{COOH}$ , but on acidifying and extracting with ether, the original methylic salt is recovered.

The change of methyloximidoxazolone into methylglyoximecarboxylic acid has been studied by means of conductivity determinations; the change is unimolecular and proceeds rapidly at first, even at  $0^\circ$ , but is not complete even after several months, since the solution always develops the red colour of the erythro-salt on adding ammonia; the equilibrium which therefore exists between the two acids can also be reached in the other direction, for a colourless alkaline solution of the open-chain acid, when acidified and subsequently neutralised with ammonia, again develops the red colour of the erythro-salt.

The formation of erythro-ions from methyloximido-oxazolone is shown by the pink tint of the aqueous solution, which becomes very marked on warming the solution, but diminishes again on cooling; the colour is also diminished by the addition of acids, or of alcohol, which would tend to drive back the dissociation; the substance thus affords an example of 'ionisation-isomerism' (this vol., i, 400). The increase of colour is accompanied by an increase of conductivity from  $\mu_{32} = 4.1$  at  $0^\circ$  to  $11.7$  at  $25^\circ$  and  $17.5$  at  $35.5^\circ$ ; the temperature coefficients are  $C_{0^\circ-25^\circ} = 0.0742$  and  $C_{0^\circ-35^\circ} = 0.1060$ , whilst lævulinic acid, a true acid of approximately equal strength, gave  $C_{0^\circ-25^\circ} = 0.0283$  and  $C_{0^\circ-35^\circ} = 0.0277$ ; the high temperature-coefficient of the oxazolone, increasing with rising temperature, is an indication that it is a 'pseudo-acid.' On the other hand, the conductivity of the red potassium salt is quite normal; from the values obtained, the dissociation constants of the oxazolone are calculated to be  $0.00080$  at  $0^\circ$ ,  $0.00347$  at  $25^\circ$ , and  $0.00586$  at  $35.5^\circ$ , whilst lævulinic acid gave the values  $0.00211$ ,  $0.00239$ , and  $0.00229$ ; the rapid increase of dissociation with temperature is again an indication of a pseudo-acid. On adding hydrochloric acid to an equivalent quantity of the red potassium salt, the colour immediately disappears and the solution has a constant conductivity, showing that the erythro-ion and the hydrogen ion combine instantly to form the colourless pseudo-acid; the phenomena of 'gradual neutralisation' cannot therefore be observed.

Phenyloximido-oxazolone forms a *hydrate* to which the formula  $\text{NOH} : \text{C} \begin{array}{c} \text{C}(\text{OH})_2 \\ \diagup \quad \diagdown \\ \text{CPh} : \text{N} \end{array} \text{O}$ , is assigned, but the whole of the water is lost

in 24 hours in a desiccator. It forms a yellow *acid potassium* salt and a violet *neutral potassium* salt; the latter gives a violet solution, which gradually loses its colour, and acquires a smell of bitter almond oil. The *silver* salt is red and explosive. The *methylic* salt separates from light petroleum in yellow crystals and melts at 95—96°; it dissolves in caustic soda to a colourless solution from which the original ether can be recovered by acidifying and extracting with ether. The alcoholic and ethereal solutions of phenyloximido-oxazolone are yellowish, but the aqueous solution has a reddish tint, especially when warm; the appearance of a violet colour on the addition of alkalis is sufficiently sensitive to serve as an indicator for titrating acid and alkali. The conversion of the oxazolone into an open-chain acid is much more rapid than in the previous case, and it is not therefore possible to determine its conductivity; the violet potassium salt has a normal conductivity, and is not hydrolysed at all.

Methylic pseudoviourate,  $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} : \text{NOMe}$ , crystallises from light petroleum in colourless flakes, decomposes at 270°, dissolves in all ordinary solvents, and slightly in water and alkalis, with a pale yellow colour. Viouric acid gives a colourless solution in alcohol, but contrary to the statement of Magnanini, shows a violet colour when dissolved in the purest water, especially on warming. The conductivity also increases with the temperature from  $\mu_{32} = 4.7$  at 0° to 7.8 at 14.5°, 10.4 at 25°, 13.3 at 35.5°, and 18.8 at 54.1°; the temperature coefficients are  $C_{0^\circ-14.5^\circ} = 0.0456$ ,  $C_{0^\circ-25^\circ} = 0.0485$ ,  $C_{0^\circ-35.5^\circ} = 0.0516$ ,  $C_{0^\circ-54.1^\circ} = 0.0555$ , whilst lævulinic acid gives decreasing values, 0.0297, 0.0293, 0.0277, 0.0249. The dissociation constants are 0.00144 at 0°, 0.00273 at 25°, and 0.00333 at 35.5°, whilst lævulinic acid gives 0.00211, 0.00228 and 0.00229. The abnormal temperature coefficients of conductivity and the rapid change in the degree of dissociation show that viouric acid is not a true acid but a pseudo-acid.

Similar phenomena to those described in the paper are also observed with the oximido-imidazolones,  $\text{NOH} : \text{C} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CR} = \text{N} \end{smallmatrix}$  and the so-called nitroso-hydantoin,  $\text{NOH} : \text{C} \begin{smallmatrix} \text{CO} - \text{NH} \\ \text{S} \cdot \text{C}(\text{NH}) \end{smallmatrix}$ , which also contain the group  $-\text{C}(\text{NOH}) \cdot \text{CO}-$ , but open-chain compounds such as isonitrosoacetone,  $\text{COMe} \cdot \text{CH} : \text{NOH}$ , and isonitrosoacetophenone give only yellow salts, and do not show the red to violet tints observed with cyclic oximidoketones. Of the three possible formulæ for the erythro-salts,  $\begin{smallmatrix} -\text{C} \cdot \text{N} \cdot \text{OK} \\ -\text{C} \cdot \text{O} \end{smallmatrix}$ ,  $\begin{smallmatrix} -\text{C} = \text{N} \\ -\text{C}(\text{OK}) \cdot \text{O} \end{smallmatrix}$ ,  $\begin{smallmatrix} -\text{C} \cdot \text{NO} \\ -\text{C} \cdot \text{OK} \end{smallmatrix}$ , the second is adopted as the most probable, corresponding with Hantzsch's formula for the erythronitrolic acids.

T. M. L.

**Narcotine and Narceine.** By GEORGE BELL FRANKFORTER and FRANK H. KELLER (*Amer. Chem. J.*, 1899, 22, 61—67).—Roser (*Annalen*, 1888, 247, 168) has stated that dimethyltolueneazammonium silver iodide,  $\text{C}_7\text{H}_6\text{Me}_2\text{N}_3\text{I} \cdot 2\text{AgI}$  (Zincke and Lawson, *Annalen*, 1886, 240, 128), is formed in converting narcotine into narceine; the compound obtained from narcotine, however, melts at 184—186°,

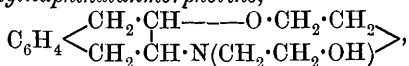
whilst that of Zincke and Lawson melted at 128—130°. The authors' analyses indicate that the substance obtained by Roser, if an azimido-compound, probably has the composition  $C_7H_6Me_2N_3Cl, 2AgI$ .

A better method than that given by Roser for converting narcotine methiodide into the methochloride, and thence into narceine, consists in adding chlorine water to its alcoholic solution; a brown, micro-crystalline precipitate of *di-iodonarcotine methiodide*,  $C_{22}H_{21}I_2NO_7, MeI$ , is obtained, whilst narcotine methiodide passes into solution, and can be isolated by evaporation. The action apparently takes place nearly quantitatively. *Di-iodonarcotine methiodide* crystallises from methylic or ethylic alcohol in slender needles, melts at 149°, and is converted by heating with an excess of chlorine water into *di-iodomethylnornarcotine methiodide*,  $C_{20}H_{27}I_2NO_7, MeI$ , which crystallises from alcohol in reddish-brown, monoclinic crystals and melts at 186°; in this conversion, it is probable that the methoxyl group which is present in the isoquinoline nucleus remains intact.

W. A. D.

**Morpholine Bases: Naphthalanmorpholine.** By LUDWIG KNORR (*Annalen*, 1899, 307, 171—187. Compare Abstr., 1898, i, 601, and this vol., i, 463).—Naphthalanmorpholine forms prisms which melt at 62—63°, and boils at 312° under 754 mm. pressure; it is not very volatile in steam, and the aqueous solution is strongly alkaline. The *hydrochloride* crystallises in prisms and melts at 275°; the *platinochloride*, *aurichloride*, and *picrate* melt and decompose at 225°, 225°, and 250° respectively. The *nitrosamine* crystallises from absolute alcohol in flattened needles and melts at 161°; the *benzoyl* derivative forms leaflets melting at 194°.

1''-Hydroxyethylnaphthalanmorpholine,



prepared by heating naphthalanmorpholine with excess of ethylenic oxide at 100°, crystallises from water and from acetone; it melts at 105—108°, and boils at about 300° under 160 mm. pressure. It is likewise produced by the action of hot, 60 per cent. sulphuric acid on dihydroxyethylamidotetrahydro-β-

naphthol,  $C_6H_4 \begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{OH} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{N}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH})_2 \end{array}$ , prepared by heating tetrahydronaphthylene oxide with diethanolamine. The *aurichloride*, *picrolonate*, and *platinochloride* decompose at 213°, 245°, and 235° respectively.

1''-Methylnaphthalanmorpholine, obtained from tetrahydronaphthylene oxide and ethanolmethylamine, melts at 57—58° and boils at 317° under 752 mm. pressure; the *hydrochloride* crystallises from alcohol in nodules, and the *platinochloride* forms octahedra or cubes, and melts at 250°, when it decomposes. The *aurichloride* and *picrate* melt at 235° and 206—208° respectively, whilst the *picrolonate* forms a yellow precipitate which dissolves very sparingly in water; the methiodide crystallises from water in flattened needles. The aqueous solution of methylnaphthalanmorpholinemethylhydroxide is strongly alkaline, and yields a precipitate with the usual reagents for alkaloids; the *picrate* melts at about 206—208°, the *platinochloride* crystallises in octahedra, and the *aurichloride* in long, flattened needles. On



evaporating a concentrated aqueous solution of the ammonium base, it is resolved into naphthalene and ethanoldimethylamine, the intermediate product being the dihydro- $\beta$ -naphthol ether of ethanoldimethylamine; this change is analogous to the conversion of codeine into the monomethyl ether of dihydroxyphenanthrene.

1''-*Ethyl-naphthalanmorpholine*, prepared from tetrahydronaphthalene oxide and ethanoethylamine, boils at 322° under 755 mm. pressure; the *hydrochloride* crystallises from alcohol in prisms and melts at 237—238°. The *picrolonate* and *platinochloride* decompose at 235° and 220° respectively; the *methiodide* dissociates at 205°. M. O. F.

**Morpholine Bases of the Camphor Series.** By LUDWIG KNORR and PAUL DUDEN (*Annalen*, 1899, 307, 187—199).—The cyclic bases obtained by intramolecular elimination of water from hydroxyethyl derivatives of amidocamphor and of methylamidocamphor are called *camphenemorpholines* by the authors; reduction adds two atoms of hydrogen, giving rise to *camphanemorpholines*.

*Dihydroxyethylamidocamphor*,  $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{N}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH})_2 \\ \diagup \text{CO} \end{smallmatrix}$ , prepared by heating amidocamphor with some excess of ethylenic oxide in sealed tubes at 100—110° during 14 hours, is a viscous, brownish oil which dissolves readily in cold, but is sparingly soluble in hot, water; it is only slightly volatile in steam, and reduces Fehling's solution vigorously when heated. The *picrate* crystallises from alcohol in thin, quadratic leaflets and melts at 139—140°, when it decomposes.

*Hydroxyethylcamphenemorpholine*,  $C_8H_{14} \begin{smallmatrix} \text{C} \text{---} \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \diagup \text{C} \cdot \text{N}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}) \end{smallmatrix}$ , prepared by heating dihydroxyethylamidocamphor with 40 per cent. sulphuric acid or 20 per cent. hydrochloric acid at 120—130° during 6 hours, is a pale yellow oil which boils at 205—210° and 240° under 70 mm. and 240 mm. pressures respectively; it is indifferent towards Fehling's solution. The *picrate* melts at 127°, and the *hydriodide* crystallises in nacreous leaflets melting at 169—170°.

*Camphenemorpholine*,  $C_8H_{14} \begin{smallmatrix} \text{C} \text{---} \text{O} \text{---} \text{CH}_2 \\ \diagup \text{C} \cdot \text{NH} \cdot \text{CH}_2 \end{smallmatrix}$ , obtained by heating amidocamphor with 1 mol. of ethylenic oxide, and distilling the crude product under atmospheric pressure, is an alkaline, secondary base which boils at 241—243° under 751 mm. pressure; it has an intense, sweet odour and is indifferent towards hot Fehling's solution. The *picrate* crystallises from alcohol in prisms or pyramids and decomposes at 196—198°.

*Methylcamphenemorpholine*,  $C_8H_{14} \begin{smallmatrix} \text{C} \text{---} \text{O} \text{---} \text{CH}_2 \\ \diagup \text{C} \cdot \text{NMe} \cdot \text{CH}_2 \end{smallmatrix}$ , prepared by heating methylamidocamphor with 1 mol. of ethylenic oxide, and distilling the product under atmospheric pressure, boils at 240—241° under 753 mm.; it is indifferent towards Fehling's solution, but the pale yellow base darkens on exposure to air, and exhibits greenish fluorescence. The *picrate* and *platinochloride* decompose at 208° and 204—205° respectively; the *methiodide* crystallises in prisms and melts at 194°.

*Methylcamphenemorpholine*,  $C_8H_{14}$   $\begin{matrix} \text{CH-O-CH}_2 \\ | \quad | \\ \text{CH} \cdot \text{NMe} \cdot \text{CH}_2 \end{matrix}$ , obtained by reducing methylcamphenemorpholine with alcohol and sodium, crystallises from petroleum in slender needles, and from water in prisms; it melts at  $101^\circ$  and boils at  $252\text{--}254^\circ$ . The *hydrochloride* forms long, slender needles and sublimes when heated, whilst the *hydriodide* decomposes above  $250^\circ$ ; the *picrate* melts at  $195^\circ$ , and the *methiodide*, which crystallises from water in lustrous, quadratic leaflets, dissociates at  $250^\circ$  without fusion. The ammonium base yields a *platinochloride* which crystallises from dilute hydrochloric acid in short prisms and decomposes at  $127^\circ$ .  
M. O. F.

**1:3-Methylmorpholone, a Basic  $\delta$ -Lactone.** By LUDWIG KNORR and EDUARD KNORR (*Annalen*, 1899, **307**, 199—206. Compare Abstr., 1898, i, 601).—The ready conversion of diethanolamine into morpholine (*loc. cit.*) has suggested the possibility of preparing morpholone,  $\text{NH} \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \text{—CO} \end{matrix} \text{O}$ , from hydroxyethylamidoacetic acid, but the production of this substance and its transformation into the basic lactone present considerable difficulty; attention has been therefore paid to the methyl derivatives.

*Hydroxyethylmethylamidoacetic acid (hydroxyethylsarcosine)*,  
 $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared by heating sarcosine with excess of ethylenic oxide at  $80\text{--}90^\circ$  during 24 hours, crystallises in deliquescent needles and melts at  $132\text{--}133^\circ$ ; the *copper* salt is anhydrous and forms deep blue plates.

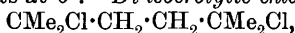
**1:3-Methylmorpholone**,  $\text{NMe} \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \text{—CO} \end{matrix} \text{O}$ , prepared by heating the hydroxy-acid, boils at  $233^\circ$  under 755 mm. pressure; the *hydrochloride* is crystalline, but is exceedingly hygroscopic, and the *picrate* melts at  $190\text{--}192^\circ$ . The *methiodide* crystallises from absolute alcohol and decomposes at about  $228^\circ$ ; it yields an *aurichloride* which forms slender needles and melts at  $205\text{--}207^\circ$ .  
M. O. F.

**Antipeptone.** By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1899, **27**, 335—347).—By the tryptic digestion of proteid, antipeptone is formed. It is not precipitable by ammonium sulphate; it gives a strong biuret, but not Millon's, reaction, and is free from sulphur. In opposition to Kutscher (this vol., i, 179), who regards antipeptone as a mixture of several substances, it is stated that antipeptone of constant composition can be prepared from impure antipeptone by treating it with alcohol. It can also be prepared pure by precipitation with iron salts in a solution saturated with ammonium sulphate.  
W. D. H.

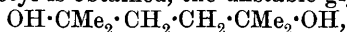
**Influence of Hydrogen Sulphide on Carbonic Oxide Blood.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, **27**, 319—323).—In opposition to Harnack (this vol., i, 467), it is proved that carboxy-hæmoglobin is much more resistant to various reagents, including hydrogen sulphide, than is oxyhæmoglobin.  
W. D. H.

## Organic Chemistry.

**Derivatives of Di-isocrotyl and Di-isobutenyl.** By S. POGORŽELSKY (*Chem. Centr.*, 1899, i, 773—775; from *J. Russ. Chem. Soc.*, 1898, 30, 977—992).—Isobutylene, prepared by the action of alcoholic potash on isobutylic iodide, combines with bromine to form isobutylenic bromide, and this compound, when treated by Butleroff's method (*Krit. Zeit. Chem.*, 1870, 524) yields isocrotylic bromide. This boils at 91—92°, has a sp. gr. 1·3544 at 0° or 1·3254 at 16·5°, and coefficient of expansion 0·00244 between 0° and 16·5°. Di-isocrotyl, prepared by the action of sodium on isocrotylic bromide, boils at 132—134° and melts at 6°. *Di-isocrotylic chloride*,



obtained by the action of hydrogen chloride on di-isocrotyl, crystallises in elongated leaflets, melts at 64°, and is soluble in alcohol, ether, benzene, light petroleum, or chloroform; hydrogen chloride is not eliminated by the action of alcoholic potash. *Di-isocrotylic bromide* crystallises in leaflets, melts at 68·5—69°, and is soluble in alcohol, ether, benzene, light petroleum, or chloroform; it is much less stable than the chloride and gradually changes into a dark liquid of penetrating odour. By the action of dilute sulphuric acid (3 vols. acid to 2 vols. water) on di-isocrotyl or of potassium carbonate on di-isocrotylic bromide, di-isocrotylic oxide is obtained; it boils at 113° under 786 mm. pressure, has a sp. gr. 0·8272 at 0° or 0·8113 at 20°, coefficient of expansion 0·000976 between 0° and 20°, and is easily soluble in alcohol, ether, light petroleum, benzene, or chloroform. *Di-isocrotylic bromhydrin*,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ , prepared by the action of hydrogen bromide on di-isocrotylic oxide, melts at 77—78°, and, when heated, decomposes into di-isocrotylic bromide and di-isocrotylic oxide. *Di-isocrotylic iodhydrin* is much less stable than the bromhydrin and melts at 70—71°. By the action of dry hydrogen chloride on di-isocrotylic oxide, the dichloride is formed. When the oxide is heated with a 1 per cent. solution of hydrochloric acid at 180—190°, di-isocrotyl is obtained, the unstable glycol,



being probably an intermediate product of the reaction. Di-isocrotylic oxide is not affected by heating with water at 190—195°.

*Di-isobutenyl*,  $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2$ , prepared by the action of sodium on isobutenylic chloride, boils at 113—114° and when heated with sulphuric acid yields di-isocrotylic oxide, the change in this case being also due to the formation of the unstable glycol. By the action of hydrogen bromide on di-isobutenyl, di-isocrotylic bromide is formed.

E. W. W.

**Hydrocarbon,  $\text{C}_{10}\text{H}_{18}$ , prepared from Active Amylic Alcohol and its Derivatives.** By A. WASSILÉEF (*Chem. Centr.*, 1899, i, 775—776; from *J. Russ. Chem. Soc.*, 1898, 30, 993—997).—Amylic iodide, prepared from active amylic alcohol, when treated with

potassium hydroxide, yields  $\alpha$ -methylethylethylene,  $\text{CMeEt}\cdot\text{CH}_2$ , boiling at  $31-34^\circ$ . This readily combines with bromine, forming the bromide,  $\text{CMeEtBr}\cdot\text{CH}_2\text{Br}$ , which has a sp. gr. 1.6921 at  $0^\circ$  and 1.6638 at  $21^\circ$ .  $\beta$ -Brom- $\alpha$ -methylethylethylene,  $\text{CMeEt}\cdot\text{CHBr}$ , obtained by the action of alcoholic potash on the bromide, boils at  $117-118^\circ$  under 767.7 mm. pressure, and has a sp. gr. 1.2668 at  $0^\circ$  and 1.2423 at  $20^\circ$ . A hydrocarbon,  $\text{C}_{10}\text{H}_{18}$ , is obtained by treating the bromamylene with sodium; it boils at  $167-170^\circ$ , and by the action of dilute sulphuric acid (3 vols. of acid to 1 of water) forms the corresponding ditertiary- $\gamma$ -oxide,  $\text{CMeEt}\cdot\text{CH}_2$   
 $\text{CMeEt}\cdot\text{CH}_2 > \text{O}$ , probably by means of the intermediate production of the glycol. The oxide boils at  $159-161^\circ$ , has a pleasant, camphor-like odour, and, by the action of hydrogen bromide dissolved in light petroleum, yields a compound,  $\text{C}_{10}\text{H}_{20}\text{Br}_2$ . E. W. W.

**Action of Zinc Dust on Alcoholic Solutions of  $\alpha$ -Halogen-substituted Alcohols and of Zinc Shavings on Alcoholic Solutions of their Acetates.** By ŽIVOIN JOČITSCH and ALEXEI FAWORSKY (*Chem. Centr.*, 1899, i, 777-778; from *J. Russ. Chem. Soc.*, 1898, 30, 998-1003. Compare this vol., i, 748, and Mokiewsky, this vol., i, 729).—The best yields of  $\alpha$ -dihalogen-substituted ethylenes are obtained by treating the alcoholic solutions of the acetates of  $\alpha$ -trihalogen-substituted alcohols with zinc shavings. Under these conditions, trichlorethyllic acetate,  $\text{COMe}\cdot\text{OCH}_2\cdot\text{CCl}_3$ , forms unsymmetrical dichloroethylene,  $\text{CCl}_2\cdot\text{CH}_2$ , and a small quantity of a gas which combines with bromine, and is probably chlorovinyl. Trichloropropyllic acetate,  $\text{COMe}\cdot\text{OCHMe}\cdot\text{CCl}_3$ , yields  $\alpha$ -dichloropropylene,  $\text{CCl}_2\cdot\text{CHMe}$ , which boils at  $76.5^\circ$ , has a sp. gr. 1.2030 at  $0^\circ/0^\circ$  and 1.1764 at  $19.5^\circ/0^\circ$ . Acetonechloroform acetate,  $\text{COMe}\cdot\text{OCMe}_2\cdot\text{CCl}_3$ , gives 85 per cent. of  $\alpha$ -dichlorisobutylene,  $\text{CCl}_2\cdot\text{CMe}_2$ , which boils at  $107.5-108.5^\circ$ , and has a sp. gr. 1.1697 at  $0^\circ/0^\circ$  and 1.1449 at  $20^\circ/0^\circ$ . Trichloromethylphenylcarbinol acetate,  $\text{COMe}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CCl}_3$ , yields 90 per cent. of dichlorostyrene, which boils at  $220-222^\circ$ , has a sp. gr. 1.2678 at  $0^\circ/0^\circ$  and 1.2499 at  $19^\circ/0^\circ$ , and tribromomethylphenylcarbinol acetate gives monobromostyrene,  $\text{CHBr}\cdot\text{CHPh}$ , which boils at  $218-220^\circ$  and has a sp. gr. 1.4482 at  $0^\circ/0^\circ$  and 1.4289 at  $19^\circ/0^\circ$ . E. W. W.

**Purification and Preservation of Chloroform.** By V. MASSON (*J. Pharm.*, 1899, [vi], 9, 568-572).—Methods are described for the purification and preservation of chloroform for anæsthetic purposes. Poppy seed oil possesses in a remarkable degree the property of preventing pure chloroform from undergoing any change. A specimen of pure chloroform which contained 1 part of the oil in 1000 parts, and had been exposed to both diffused light and direct sunlight, remained quite pure for 3 years. H. R. LE S.

**Action of Bromine on Isobutylic Bromide in presence of Aluminium Bromide and Chloride.** By A. MOUNEYRAT (*Compt. rend.*, 1899, 129, 226-228).—When bromine acts on isobutylic bromide in presence of aluminium bromide, the products are (1) a small quantity of isobutylenic bromide, (2) a large quantity of the tribromisobutane,  $\text{CMe}_2\text{Br}\cdot\text{CHBr}_2$ , a colourless liquid of sp. gr. 2.188 at  $16^\circ$ , which boils

at 110—114° under 15 mm. pressure, (3) small quantities of an isomeric tribromisobutane, and a tetrabromisobutane. No variations in the relative proportions of isobutylic bromide and bromine led to a satisfactory yield of isobutylenic bromide. If, however, a small quantity of aluminium chloride is used instead of the bromide, the isobutylenic bromide,  $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$ , which boils and decomposes at 148—149° under normal pressure, is obtained in quantity amounting to 50—55 per cent. of the calculated yield.

Tribromisobutane,  $\text{CMe}_2\text{Br}\cdot\text{CHBr}_2$ , when treated with bromine in presence of aluminium chloride or bromide, yields 65—70 per cent. of the theoretical yield of tetrabromisobutane,  $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CHBr}_2$ ; this has a sp. gr. 2.557 at 16°, and boils at 159—163° under 12 mm. pressure.  
C. H. B.

**Action of Sulphuric Acid on Nitroheptane.** By R. A. WORSTALL (*Amer. Chem. J.*, 1899, 22, 164—167).—When nitroheptane is heated with dilute sulphuric acid at 80° for 10 minutes, or is gradually mixed with an excess of concentrated sulphuric acid (sp. gr. 1.84) at the ordinary temperature, it is converted into heptoic acid, but when added to five times its weight of well-cooled, fuming sulphuric acid, there is formed, in addition to heptoic acid, a small quantity of *nitroheptanesulphonic acid*, the *barium* salt,  $(\text{NO}_2\cdot\text{C}_7\text{H}_{14}\cdot\text{SO}_3)_2\text{Ba}$ , of which is easily soluble in water and in hot alcohol, and crystallises from the latter in small plates.  
W. A. D

**A Colour Reaction of Vinylic Alcohol.** By ENRICO RIMINI (*Gazzetta*, 1899, 29, i, 390—393).—After shaking cheese with concentrated hydrochloric acid to dissolve the casein, gentle heating and shaking with a few drops of ether in some cases produces an azure-violet coloration, the intensity of which varies with the sample of ether employed; pure ether, recently distilled over lime and sodium, gives no colour. The author finds that the formation of this colour is due to the presence of vinylic alcohol in the ether. Further, Liebermann's reaction for proteids, namely, the production of an azure-violet, when the proteid, after boiling with alcohol and washing with ether, is heated with concentrated hydrochloric acid, fails if ether containing no vinylic alcohol is employed.  
T. H. P.

**Oxidation of Propylenic Glycol by Bromine Water.** By ANDRÉ KLING (*Compt. rend.*, 1899, 129, 219—220).—Acetol,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\text{OH}$ , is formed when propylenic glycol is mixed with a molecular proportion of bromine dissolved in water and the mixture is exposed to sunlight.  
C. H. B.

**Formation of a Sugar from Egg Albumin.** By PAUL MAYER (*Chem. Centr.*, 1899, i, 687; from *Deutsch. Med. Woch.*, 25, 95—97).—Egg albumin was prepared in the form of a white powder, free from glucose, by removing the fat from yolk of egg by means of ether, and then treating with water and alcohol. By boiling this substance with a 4—5 per cent. solution of hydrochloric acid for 6 hours according to Krawkow's method (*Pflüg. Arch.*, 65, 281), a carbohydrate was obtained, which dissolved in glacial acetic acid, forming a lævo-

rotatory solution and yielded an osazone melting at  $203^{\circ}$ . Analysis showed it to be a hexose, and the properties of its osazone are identical with those of glucosazone.

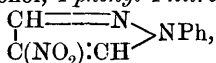
E. W. W.

**Colour Reactions of Oxycellulose.** By EDMOND JANDRIER (*Compt. rend.*, 1899, 128, 1407—1408).—The oxycelluloses, and especially that obtained by the oxidation of cotton with potassium chlorate (Vignon's process), yield colour reactions when a solution or suspension is mixed with a phenol, and concentrated sulphuric acid is added so that it forms a layer below the organic mixture; the coloration is developed at the junction of the liquids. A golden yellow is produced with phenol; varying shades of violet are obtained with  $\alpha$ -naphthol, menthol, thymol, and the alkaloids morphine and codeine;  $\beta$ -naphthol, quinol, and resorcinol give brown shades, and gallic acid gives a green coloration at the junction, which changes to violet in the sulphuric acid. Formaldehyde, gum arabic, and the aldoses give colour reactions when similarly treated.

G. T. M.

**Nitromalonic Aldehyde.** By HENRY B. HILL and JOSEPH TORREY, jun. (*Amer. Chem. J.*, 1899, 22, 89—110).—The authors find that the colourless compounds,  $C_3H_2NO_4K + H_2O$  and  $C_3H_2NO_4Na + H_2O$ , obtained respectively as final products of the action of potassium and sodium nitrite on mucobromic acid (Hill and Sanger, *Abstr.*, 1883, 47), are salts of *nitromalonic aldehyde*,  $CHO \cdot CH(NO_2) \cdot CHO$ . This aldehyde, obtained by adding an ethereal solution of hydrogen chloride to the silver salt suspended in absolute ether, crystallises from light petroleum in feathery aggregates of prisms and melts at  $50$ — $51^{\circ}$ ; its molecular weight was determined cryoscopically, using benzene as the solvent. In aqueous solutions, it is slowly decomposed at the ordinary temperature, more rapidly at  $45$ — $50^{\circ}$ , giving rise to 1:3:5-trinitrobenzene and formic acid. The *anil*,  $C_3H_3NO_3 \cdot NPh$ , obtained on adding aniline hydrochloride to an aqueous solution of the sodium salt, crystallises from alcohol in lustrous, yellow scales, and melts at  $143$ — $144^{\circ}$ ; if aniline is employed instead of its hydrochloride, the *dianil*,  $C_3H_3NO_2(NPh)_2$ , is obtained in the form of brilliant yellow needles. The *paratolils*,  $C_{10}H_{10}N_2O_3$ , and  $C_{17}H_{17}N_3O_2$ , prepared similarly from paratoluidine, melt respectively at  $176$ — $177^{\circ}$  and  $138^{\circ}$ .

The *phenylhydrazone*,  $C_9H_9N_3O_3$ , formed on adding phenylhydrazine hydrochloride to a solution of sodium nitromalonic aldehyde, forms yellow needles and melts and decomposes at about  $101^{\circ}$ ; the *diphenylhydrazone*,  $C_{15}H_{15}N_5O_2$ , obtained by adding dilute alcoholic phenylhydrazine to the sodium derivative of the aldehyde and passing carbonic anhydride through the solution, is a dark-red, unstable, crystalline substance which melts and decomposes at about  $98^{\circ}$ , and yields a stable, crystalline *sodium* derivative,  $C_{15}H_{14}N_5O_2Na$ , and a *lead* salt,  $(C_{15}H_{14}N_5O_2)_2Pb$ . When either of the phenylhydrazones is heated, alone or with alcohol, 1-phenyl-4-nitropyrazole,



is obtained; this crystallises from alcohol in slender, slightly coloured, prismatic clusters, from light petroleum in white, silky needles, and

melts at 126—127°. 4-Nitropyrazole (Buchner and Fritsch, *Abstr.*, 1893, i, 432; and Knorr, *Annalen*, 1894, 279, 228) is obtained when the product of the action of hydrazine sulphate (2 mols.) on nitromalonic aldehyde is heated with moderately concentrated hydrochloric acid; this melted at 157—158° (162° corr.) and its production affords a proof of the structure of the aldehyde.

$\beta$ -Nitroisoxazole,  $C_3H_2N_2O_3$ , formed on adding hydroxylamine hydrochloride (1 mol.) to concentrated, aqueous sodium nitromalonic aldehyde, crystallises from a mixture of ether and light petroleum in aggregates of transparent, rhombic plates, and melts at 46—47°; if this action is carried out in presence of an equivalent quantity of sodium carbonate or sodium hydroxide, transparent, yellow crystals of the sodium derivative,  $C_3H_4N_3O_4Na$ , of nitromalonic dialdoxime are obtained; the corresponding silver salt,  $C_3H_4N_3O_4Ag$ , is a pale yellow, microcrystalline powder; the dioxime could not be isolated. Nitromalonic aldehyde aniloxime,  $NPh\cdot CH\cdot CH(NO_2)\cdot CH\cdot N\cdot OH$ , formed on adding aniline hydrochloride to a solution of the sodium derivative of the dioxime, crystallises from alcohol in yellow, globular aggregates, and melts at 162°; it can also be obtained by acting with hydroxylamine on the monanil of nitromalonic aldehyde (m. p. 143—144°).

In alkaline solution, nitromalonic aldehyde readily condenses with acetone to form paranitrophenol, and similar condensation products are formed with ketonic acids and other ketones. W. A. D.

**Azelaone.** By W. MILLER and A. TSCHITSCHKIN (*Annalen*, 1899, 307, 375—383. Compare Mager, *Abstr.*, 1893, i, 558, and Derlon, *Abstr.*, 1898, i, 638).—The best yield of azelaone is obtained when small quantities of azelaic acid are distilled with an equal weight of soda lime; it boils at about 205°. The gaseous products of the distillation, when passed through bromine, formed erythrene tetrabromide,  $CH_2Br\cdot CHBr\cdot CHBr\cdot CH_2Br$ , together with ethylenic and propylenic dibromides. M. O. F.

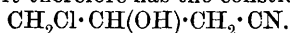
**Acetylacetonates [Metallic Derivatives of Acetylacetone].** By G. URBAIN and A. DEBIERNE (*Compt. rend.*, 1899, 129, 302—305. Compare *Abstr.*, 1897, i, 236).—The compounds of acetylacetone with the sesquioxides crystallise in similar forms, melt without decomposition, and are more or less volatile; when crystallised from chloroform, they all retain 2 mols. of the solvent; their molecular weights, determined by cryoscopic methods, correspond with those required for the simple formula  $R(CHAc_2)_3$ .

The ferric derivative,  $Fe(CHAc_2)_3$ , prepared by digesting ferric hydroxide with excess of acetylacetone, forms a bright red, crystalline precipitate almost insoluble in water; it is soluble in the ordinary organic solvents, can be crystallised from benzene and melts at 184°. The manganic derivative crystallises from ether in shining, black crystals and melts at 172°. The cobaltic derivative melts at 240°, and is more stable than the preceding salts; its solutions in organic solvents are intensely green, and it separates from these in black crystals. The chromic derivative is a reddish-violet salt melting at 214° and boiling at 340° without decomposition; the vapour is green.

The *aluminic* derivative cannot be easily obtained from the hydroxide; it is, however, readily prepared from the anhydrous chloride. The *nickelic* derivative could not be isolated.

G. T. M.

**Dichlorobutyric Acid (Dichloro-3:4-butanoic Acid).** By ROBERT LESPIEAU (*Compt. rend.*, 1899, 129, 224—225).—The chloronitrile obtained by the action of potassium cyanide on epichlorhydrin (this vol., i, 243) yields crotonic acid (m. p. 72°) on careful reduction with hydriodic acid; it therefore has the constitution



When treated with phosphorus pentachloride, it yields a *dichloronitrile*,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CN}$ , which boils at 113—114° under 25 mm. pressure, and has a sp. gr. 1.314 at 0°. *βγ-Dichlorobutyric acid*,  $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{COOH}$ , obtained from the nitrile by hydrolysis, melts at 49—50°; its *ethylic* salt boils at 206—209° under 750 mm., and at 92° under 14 mm. pressure.

C. H. B.

**Identification and Separation of Fatty Acids by means of Tetrachloroquinol.** By LOUIS BOUVEAULT (*Compt. rend.*, 1899, 129, 53—56).—The identification and separation of the fatty acids by means of the compounds which they form with tetrachloroquinol is attended with considerable advantages, the amides, anilides, paratoluidides, and phenylhydrazides, which have been used for these purposes, being in many cases difficult to purify, whilst the regeneration of the acids therefrom is often very troublesome. When tetrachloroquinol is heated in a reflux apparatus with excess of an acid chloride,  $\text{R}\cdot\text{CO}\cdot\text{Cl}$ , it reacts with 1 and 2 mols. of the latter to form monacid and diacid derivatives respectively. The diacid derivatives,  $\text{C}_6\text{Cl}_4(\text{O}\cdot\text{CO}\cdot\text{R})_2$ , are very soluble in ether, benzene, chloroform, hot methylic or ethylic alcohols, but less so in light petroleum, and insoluble in water. They are stable, well crystallised substances, which are not acted on by dilute acids and alkalis; warm alcoholic potash rapidly hydrolyses them with regeneration of the acid. The monacid derivatives,  $\text{OH}\cdot\text{C}_6\text{Cl}_4\cdot\text{O}\cdot\text{CO}\cdot\text{R}$ , are also well crystallised, and are distinguished from the preceding compounds by their solubility in dilute alkalis; they are also more soluble in alcohol, and less soluble in light petroleum than the diacid derivatives. The diacid derivatives of acetic (245°), propionic (160°), butyric (137°), and *α*-dimethylisocrotonic (130—134°) acids have the melting points indicated; the monacid derivative of the last named acid melts at 132°.

N. L.

**Action of Pyruvic Acid on Malonic Acid: Synthesis of Itaconic Acid.** By KARL GARZAROLLI-THURNLACKH (*Monatsh.*, 1899, 20, 467—479).—When pyruvic and malonic acids, in molecular proportion, are dissolved in glacial acetic acid and the solution is warmed on a water-bath until carbonic anhydride is no longer evolved, itaconic and citramalic acids are obtained, the former being the principal product. A third acid, isomeric with citramalic acid, also seems to be produced, but no evidence was obtained of the formation of citraconic acid in the reaction. The production of itaconic to the exclusion of citraconic acid makes it probable that pyruvic acid reacts in the enolic



form. It is noteworthy, therefore, that, contrary to Schiff's statement (Abstr., 1898, i, 490), the pyruvic acid used, and also its condensation product with benzylideneaniline, gave a coloration with an ethereal solution of ferric chloride.

R. H. P.

**Ethyllic Azelate.** By W. MILLER (*Annalen*, 1899, 307, 384—386).—*Ethyllic azelate* is a colourless, somewhat viscous liquid, having a slight, agreeable odour, and distilling at 291—292°; its sp. gr. is 0.9906 at 0°/0° and 0.9766 at 15°/0°.

M. O. F.

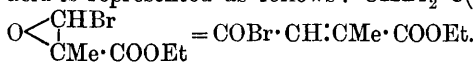
**Methylic Hydroxymethylenecyanacetate and some of its Homologues.** By E. GRÉGOIRE DE BOLLEMONT (*Compt. rend.*, 1899, 129, 50—53).—According to Claisen (Abstr., 1897, i, 592), hydroxymethylene derivatives of the type of ethylic hydroxymethyleneacetate may be regarded as formic acid in which oxygen has been replaced by a carbon atom united to two negative groups. Such compounds behave, in fact, like strong monobasic acids, and the introduction of a more negative radicle, such as cyanogen, in place of the acetyl group might be expected to lead to the formation of compounds of a still more pronouncedly acid character. The alkylic hydroxymethylenecyanacetates, obtained by hydrolysis of the corresponding methoxy- and ethoxy-methylenecyanacetates (Abstr., 1899, i, 736), have properties which show that this is the case. These compounds are strong monobasic acids which displace carbonic and acetic acids from their salts, and are converted by the action of ammonia and aniline into the corresponding amido- and anilido-methylenecyanacetates. They are slightly soluble in water, more soluble in alcohol and ether, and undergo more or less decomposition when distilled under diminished pressure. Their aqueous solutions give an intense orange-brown coloration with ferric chloride.

*Methylic hydroxymethylenecyanacetate*,  $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{COOMe}$ , is a crystalline substance of pungent odour and melts at 136—137°. The value found for its affinity coefficient ( $K = 1.505$ ) shows that it may be compared with the chloracetic acids. The *barium* salt crystallises with  $1\text{H}_2\text{O}$  and is soluble in hot water, but only slightly so in alcohol or ether; it becomes anhydrous at 150° and at the same time acquires a yellowish tint. The *copper* salt, with  $2\text{H}_2\text{O}$ , forms pale green crystals, which become anhydrous and darken in colour at 110°. The *silver* salt crystallises in silky tufts and is converted by the action of methylic iodide into methylic methoxymethylenecyanacetate. *Ethylic hydroxymethylenecyanacetate*,  $\text{OH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{COOEt}$ , was obtained as a colourless oil, and also in the form of transparent plates melting at 68—69°. *Amylic hydroxymethylenecyanacetate* could only be obtained in an impure state as an uncrystallisable oil.

N. L.

**Conversion of Alkylic Dibromacetoacetates into Mesaconic Acid and its Homologues.** By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 781—784; from *J. Russ. Chem. Soc.*, 1898, 30, 1009—1030).—The paper contains a criticism of the various theories of the mechanism of the reaction whereby alkylic dibromacetoacetates are converted into mesaconic acid and its homologues. By boiling ethylic methyl-

acetoacetate with bromine (2 mols.) and water as long as carbonic anhydride is evolved, an oil containing mono-, di-, and tri-bromo-methyl ethyl ketone is obtained. By heating this oil with a 10 per cent. solution of sodium carbonate and acidifying the product, isocrotonic acid, or probably a mixture of this acid with crotonic acid, is formed. According to Faworsky's first theory of the method of formation of unsaturated acids from dichloroketones,  $\alpha$ -bromobutyric acid should be the first product of the above reaction, but by the action of sodium carbonate this acid forms  $\alpha$ -hydroxybutyric acid, and not isocrotonic acid. Faworsky's second theory is adopted by the author, and the conversion of alkylic dibromacetoacetates into mesaconic acid is represented as follows:  $\text{CHBr}_2 \cdot \text{C}(\text{OH}) \cdot \text{CMe} \cdot \text{COOEt} - \text{HBr} =$



The intermediate unstable oxide and the acid bromide cannot be isolated, but by the action of an alcoholic instead of an aqueous solution of an alkali carbonate, the ethoxy-compound corresponding with the acid bromide may be obtained if the action is stopped before the alkali hydroxide has completely hydrolysed it. These ethoxy-compounds are also formed in large quantities by the action of alcoholic potash on alkylic dibromalkylacetoacetates at a low temperature, and may be removed by distilling in steam.

The neutral compound obtained in the preparation of dimethyl-mesaconic acid from ethylic dibromisopropylacetoacetate boils at  $240-241^\circ$ , and consists mainly of diethylic dimethylmesaconate, whilst that formed in the preparation of ethylmesaconic acid from ethylic dibromopropylacetoacetate is diethylic ethylmesaconate. By the action of alcoholic potash on ethylic dibromethylacetoacetate, an oil is formed which, when hydrolysed, yields methylmesaconic acid, and when only 2 mols. of potassium hydroxide are used, this compound is the main product of the reaction. According to the author, the boiling point of Faworsky's dichloroketone,  $\text{CMe} \cdot \text{CCl}_2 \cdot \text{CH}_2\text{Me}$ , indicates that it probably contained the compound  $\text{CMeCl}_2 \cdot \text{CO} \cdot \text{CH}_2\text{Me}$  to some extent, and this would explain the formation of both angelic and  $\alpha$ -ethylacrylic acids.

By the action of alcoholic potash on alkylic dibromalkylacetoacetates, small quantities of bye-products containing easily volatile acids which decolorise potassium permanganate are obtained; these probably result from the decomposition of ketones formed by the action of hydrogen bromide. In the case of ethylic dibromethylacetoacetate, propylideneacetic and butyric acids were identified. These syrupy acid liquids, when distilled, yield two fractions of which the one insoluble in water contains ethylic mesaconate or homologous compounds, whilst the fraction soluble in water, when distilled with steam, yields acids which are not easily volatile and are not hydroxy-acids.

By the action of an aqueous solution of potassium carbonate on ethylic dibromacetosuccinate, an acid, which is probably aconitic acid, is practically the only product, whilst by the action of an alcoholic solution of potassium hydroxide, the following at least are formed:

fumaric acid, a dimorphous, crystalline acid which melts at 185—190°, aconitic acid, and a syrupy acid. E. W. W.

**Synthesis of Lævulinic Acid.** By EDMOND E. BLAISE (*Bull. Soc. Chim.*, 1899, [iii], 21, 647—650. Compare this vol., i, 331).—Carbethoxypropionic chloride,  $\text{COOEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COCl}$ , reacts with zinc methyl in benzene solution to form ethylic lævulinate. The *semicarbazone*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{ON} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ , obtained from lævulinic acid, crystallises from boiling alcohol in slender needles melting at 187°. N. L.

**Homologues of Mesaconic, Citraconic, and Itaconic Acids.** By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 780—781; from *J. Russ. Chem. Soc.*, 1898, 30, 1003—1009. Compare *J. Russ. Chem. Soc.*, 23, 430).—A yield of 35—40 per cent. of dimethylmesaconic acid (Demarçay's oxyisohexinic acid) is obtained by decomposing ethylic dibromisopropylacetoacetate with sufficient alcoholic potash to render the mass permanently alkaline. The acid is purified by converting it into the diethylic salt which boils at 239—240°, and is easily hydrolysed by alkalis, but only partially by a 50 per cent. solution of sulphuric acid. The acid melts at 186°; the calcium salt,  $\text{C}_7\text{H}_8\text{O}_4\text{Ca} + 2\text{H}_2\text{O}$ , crystallises from water in small prisms, and the silver salt,  $\text{C}_7\text{H}_8\text{O}_4\text{Ag}_2$ , in needles.

Dimethylcitraconic anhydride, prepared by heating dimethylmesaconic acid with acetic chloride (2 mols.) at 110°, boils at 138° under 61 mm. pressure, melts at 5·25°, has a sp. gr. 1·1425 at 0°/0°, and dissolves easily in water, forming a solution which decomposes carbonates and, when evaporated, yields the original anhydride. Calcium dimethylcitraconate,  $\text{C}_7\text{H}_8\text{O}_4\text{Ca} + \text{H}_2\text{O}$ , crystallises from water in plates, and the barium salt,  $\text{C}_7\text{H}_8\text{O}_4\text{Ba} + 1\frac{1}{2}\text{H}_2\text{O}$ , in small plates; the silver salt forms a powder and is very sparingly soluble in water.

Dimethylitaconic acid, obtained by heating dimethylcitraconic anhydride with 2—3 times its volume of water at 140°, crystallises from water in long prisms and from alcohol in thin, pointed plates, and melts at 154—156°. Teraconic acid, which must be identical with this acid, melts at 161—163°; when heated, however, at the rate of 4° per minute, it melts at 154—156°. Both acids, when heated with a 50 per cent. solution of sulphuric acid, yield terebic acid melting at 174—175°, and both form anhydrous barium salts.

When dimethylcitraconic anhydride or dimethylitaconic acid is heated with water at 190°, carbonic anhydride is liberated and isocapro lactone,  $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \\ | \quad \diagup \\ \text{CH}_2 \quad \text{CO} \end{array} \text{O}$ , is formed. The lactone is a neutral oil, boils at 205—206° under 753 mm. pressure, and, when warmed with baryta water, forms an amorphous barium salt which, with silver nitrate, yields silver hydroxyisocaproate. Terebic acid, when distilled with a 50 per cent. solution of sulphuric acid, forms caprolactone, hence the formation of the latter from dimethylitaconic acid might easily depend on its conversion into terebic acid, but no trace of terebic acid was found in the acid mother liquor. By heating dimethylitaconic acid with a 20 per cent. solution of sulphuric acid at

175° for 24 hours, caprolactone is obtained and ethylmesaconic acid under similar conditions also yields a lactone-like oil. E. W. W.

**Ethylic Glutaconate, I.** By FERDINAND HENRICH (*Monatsh.*, 1899, 20, 539—569).—The hydrogen of the methylene group of ethylic glutaconate,  $\text{COOEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COOEt}$ , is displaceable by alkyl radicles, owing to the influence of the adjacent  $\cdot\text{CO}\cdot$  and  $\cdot\text{CH}\cdot\text{CH}\cdot$  groups, and in this respect the compound resembles resorcinol, the diketonic formula for which also contains the  $\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot$  group (Herzig and Zeisel, *Abstr.*, 1890, 1404); the substitution, however, takes place much more readily in the glutaconate, both hydrogen atoms being displaced.

Ethylic glutaconate has a sp. gr. 1.0499 at 20°/4°; the index of refraction for sodium light is  $n_D$  1.4474; the molecular refraction is 47.27, using the formula of Lorenz and Lorentz, the calculated value being 46.87; the molecular weight, determined from the freezing point of a solution in benzene, is normal. It is hydrolysed by boiling with caustic soda, or by warming with sodium ethoxide in alcoholic solution; the *sodium* derivative,  $\text{COOEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHNa}\cdot\text{COOEt}$ , however, is precipitated as a yellow salt when dry ether is added to a freshly-prepared solution of the substance in alcoholic sodium ethoxide. It is readily oxidised by potassium permanganate, and seems to give no characteristic coloration with alcoholic or ethereal ferric chloride, although on one occasion a very pure specimen, after solution in alcoholic sodium ethoxide and precipitation with dilute sulphuric acid, gave an intense red-violet coloration.

Methylic iodide acts very vigorously on a solution of ethylic glutaconate in alcoholic sodium ethoxide; the monomethyl derivative was not isolated, but by hydrolysis of the product a mixture of acids was obtained, of which a fraction melting at 118—130° seemed to consist chiefly of monomethylglutaconic acid. *Dimethylglutaconic acid* sinters at 123° and melts at 129—130°, although it only becomes transparent at 132—133°; it dissolves readily in cold ether, alcohol, or acetic acid, less readily in benzene, toluene, chloroform, or light petroleum, and crystallises from water in beautiful, snow-white forms. It is not acted on by nitrous acid, but is oxidised by potassium permanganate, yielding dimethylmalonic acid. An amorphous substance, insoluble in toluene, was also produced in the preparation of dimethylglutaconic acid; this melted at 171—172°, with decomposition, contained C=48.55, H=5.26 per cent., and was not acted on by potassium permanganate.

*Ethylic isonitrosoglutaconate*,  $\text{COOEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{NOH})\cdot\text{COOEt}$ , prepared by the action of nitrous acid on ethylic sodioglutaconate, melts at 81—83°, crystallises from light petroleum in white needles, dissolves readily in cold benzene, chloroform, or acetone, and moderately in alcohol or acetic acid. It is strongly acid, decomposes carbonates, is soluble in alkalis with an intense yellow coloration, dissolves in hot, but not in cold, concentrated hydrochloric acid, and reduces Fehling's solution.

*Phenylazoglutaconic acid*,  $\text{COOH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{COOH})\cdot\text{N}\cdot\text{NPh}$  or  $\text{COOH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{COOH})\cdot\text{N}\cdot\text{NHPh}$ , melts at 162.5° with evolution of

gas, dissolves readily in hot, and moderately in cold alcohol, but only slightly in ether, alcohol, or acetone, or in hot benzene or chloroform, and is insoluble in light petroleum. In concentrated sulphuric acid, it forms a dark, reddish-yellow solution. The *monethylic* salt crystallises from dilute alcohol in yellow needles, melts and decomposes at  $152-153^{\circ}$ , dissolves readily in ether, chloroform, or alcohol, less readily in acetic acid, and only slightly in benzene or light petroleum; it dissolves in sulphuric acid with a reddish-yellow coloration, and gives a transient blue coloration with potassium dichromate, ferric chloride, or sodium nitrite.

Ethylic glutaconate condenses with benzaldehyde and acetaldehyde, but definite products were not isolated. T. M. L.

**Direct Conversion of Acetamide into Ethylamine by Reduction.** By GUERBET (*Compt. rend.*, 1899, 129, 61—63).—When a solution of acetamide in amyllic alcohol is boiled in a reflux apparatus with metallic sodium, one half of the acetamide is converted into ethylamine, whilst the other half is decomposed, with formation of ammonia, by the sodium hydroxide produced in the first reaction.

N. L.

**Ureides and Acylated Alkyllic Carbamates.** By HEINRICH BECKURTS (*Arch. Pharm.*, 1899, 237, 285—288).—An introduction to the two following papers. C. F. B.

**Action of Alkylsulphinates on Chloracetylurethanes and Chloracetocarbamides.** By G. FRERICHs (*Arch. Pharm.*, 1899, 237, 288—299).—By heating together chloracetic chloride,  $\text{CH}_2\text{Cl}\cdot\text{COCl}$ , and a urethane,  $\text{NH}_2\cdot\text{CO}\cdot\text{OR}$  [ $\text{R} = \text{Et}$ , *iso*-Bu, Ay], and crystallising the product from alcohol, a chloracetylurethane,  $\text{COOR}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , is obtained. When this is heated with a sulphinate,  $\text{R}'\cdot\text{SO}_2\cdot\text{Na}$  [ $\text{R}' = \text{Ph}$ , paratolyl], in alcoholic solution, a sulphonacetylurethane,  $\text{COOR}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{R}'$ , is formed. This is decomposed when heated with aqueous caustic soda into carbonic anhydride, the alcohol  $\text{R}\cdot\text{OH}$ , ammonia, and the sulphonacetic acid,  $\text{SO}_2\text{R}'\cdot\text{CH}_2\cdot\text{COOH}$ ; no doubt the first three substances result from the further action of the alkali on the urethane,  $\text{COOR}\cdot\text{NH}_2$ , first eliminated. With alcoholic caustic potash in the cold, the products are the sulphonacetic acid and the urethane, but, on boiling, these undergo further decomposition, in this case into the sulphone  $\text{R}'\cdot\text{SO}_2\cdot\text{CH}_3$  and carbonic anhydride, and into carbonic anhydride, the alcohol  $\text{R}\cdot\text{OH}$ , and ammonia respectively. The compounds prepared, and their melting points, are as follows: *Chloracetyl ethylurethane*,  $129^{\circ}$ ; *phenylsulphonacetyl ethylurethane*,  $69^{\circ}$ ; *paratolylsulphonacetyl ethylurethane*,  $103^{\circ}$ ; *chloracetyl isobutylurethane*,  $72^{\circ}$ ; *phenylsulphonacetyl isobutylurethane*,  $81^{\circ}$ ; *paratolylsulphonacetyl isobutylurethane*,  $89^{\circ}$ ; *chloracetyl amylurethane*,  $68^{\circ}$ ; *phenylsulphonacetyl amylurethane*,  $73.5^{\circ}$ ; *paratolylsulphonacetyl amylurethane*,  $83^{\circ}$ .

By heating chloracetic chloride with a carbamide, for example, methylcarbamide,  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}_2$ , a chloracetylcarbamide,



is obtained. This reacts with sulphinates as the chloracetylurethanes do,

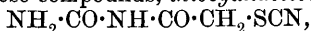
and yields sulphonacetylcarbamides,  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SO}_2\text{R}'$ . These are decomposed by alcoholic potash much in the same way as the analogous urethane derivatives; paratolylsulphonacetylmethylcarbamide, for example, yields methylcarbamide and paratolylsulphonacetic acid, or eventually methylamine, ammonia, carbonic anhydride, and paratolylmethylsulphone. The following are the compounds prepared: *Phenylsulphonacetylcarbamide*,  $225^\circ$ ; *paratolylsulphonacetylcarbamide*,  $223\text{--}224^\circ$ . *Chloracetylmethylcarbamide*,  $205^\circ$ ; *phenylsulphonacetylmethylcarbamide*,  $207^\circ$ ; *paratolylsulphonacetylmethylcarbamide*,  $220^\circ$ .  
C. F. B.

**Action of Potassium Hydrosulphide and Thiocyanate on Chloracetylurethanes and Chloracetocarbamides.** By G. FRIEDRICH (Arch. Pharm., 1899, 237, 300—331).—When a chloracetylurethane,  $\text{COOR}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$  [ $\text{R} = \text{Et}$ , *iso*-Bu, Ay], is dissolved in warm alcohol and alcoholic potassium hydrosulphide is added gradually until excess is present, potassium chloride is deposited, hydrogen sulphide is evolved, and on pouring the mixture into water a thiodiglycolylurethane,  $(\text{COOR}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2)_2\text{S}$ , separates; it was not found possible to obtain compounds of the type  $\text{COOR}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SH}$ . *Thiodiglycolyl-diethyl-*, *-di-isobutyl-*, and *-diamyl-urethanes* melt at  $187^\circ$ ,  $127^\circ$ , and  $137\cdot5^\circ$  respectively.

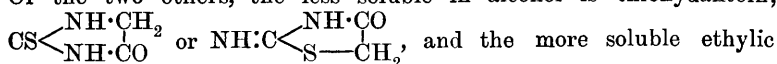
Potassium hydrosulphide reacts in a similar manner with chloracetocarbamides, for example, with  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , yielding thiodiglycolylcarbamides,  $(\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2)_2\text{S}$ . *Thiodiglycolylcarbamide* and *-dimethylcarbamide* are amorphous and decompose without melting when heated.

When chloracetylurethane is heated for a few minutes on the water-bath with potassium thiocyanate in alcoholic solution, and cold water is added gradually to the filtered solution, *thiocarbimidoacetylurethane*,  $\text{COOEt}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NCS}$ , separates; this melts at  $86^\circ$  and dissolves in hot aqueous caustic soda, yielding a red solution which evolves hydrogen sulphide when acidified. When boiled for an hour with water or dilute alcohol, it is converted into the isomeric *thiocyanacetylurethane*,  $\text{COOEt}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SCN}$ ; this melts at  $174^\circ$ , and dissolves in hot aqueous caustic soda with evolution of ammonia and formation of thioglycollic acid. *Thiocarbimido-* and *thiocyan-acetylamylurethanes* are obtained by similar methods and exhibit similar reactions; they melt at  $58^\circ$  and  $147^\circ$  respectively.

When chloracetocarbamide is boiled with potassium thiocyanate in alcoholic solution, three products are obtained in addition to potassium chloride. One of these compounds, *thiocyanacetocarbamide*,



is insoluble in alcohol and decomposes without melting when heated. Of the two others, the less soluble in alcohol is thiohydantoin,

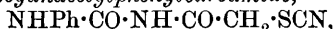


allophanate,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{COOEt}$ . Probably thiocarbimidoacetocarbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NCS}$ , is the first product, but is converted to some extent into the isomeric thiocyanacetocarbamide, whilst to a still larger extent it decomposes into thiohydantoin and

cyanic acid, the latter of which at once reacts with ethylic alcohol to form ethylic allophanate. When chloracetocarbamide and potassium thiocyanate are heated together in aqueous solution, thiohydantoin is formed as before, and carbonic anhydride evolved, but apparently no thiocyanacetocarbamide is produced; no doubt the carbonic anhydride results from the action of water on the nascent cyanic acid.

When chloracetomethylcarbamide,  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , is heated with potassium thiocyanate in alcoholic solution, a smell of methylcarbimide is observed, and thiohydantoin, together with crystalline *thiocyanacetomethylcarbamide*,  $\text{NHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{SCN}$ , can be isolated from the product; in aqueous solution the same result is obtained (it is noteworthy that methylcarbimide and thiohydantoin are formed, not carbimide and methylthiohydantoin).

When *chloracetylphenylcarbamide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$  (which is prepared from chloracetic chloride and phenylcarbamide and melts at  $160^\circ$ ) is boiled with potassium thiocyanate in aqueous solution, carbonic anhydride is evolved and diphenylcarbamide, thiohydantoin, and pulverulent *thiocyanacetylphenylcarbamide*,



are also formed; doubtless the first two result from the decomposition of "nascent" phenylcarbimide. In alcoholic solution, thiocyanacetylphenylcarbamide, thiohydantoin and phenylurethane are formed, the last doubtless as a result of the action of the alcohol on nascent phenylcarbimide; some diphenylcarbamide is obtained in this case also, due probably to the presence of water in the alcohol.

C. F. B.

**Molecular Rearrangement of Alkyl \*Thioncarbamates.** By HENRY L. WHEELER and BAYARD BARNES (*Amer. Chem. J.*, 1899, 22, 141—151).—When methylic thioncarbamate,  $\text{NH}_2\cdot\text{CS}\cdot\text{OMe}$ , is dissolved in methylic iodide (1 mol.), the solution becomes warm, and finally solidifies to a mass of crystals of methylic thiolcarbamate,  $\text{NH}_2\cdot\text{CO}\cdot\text{SMe}$ ; this crystallises from water and melts at  $107\text{--}108^\circ$ , not at  $95\text{--}98^\circ$ , as stated by Blankenhorn (*Abstr.*, 1878, ii, 215), and is also formed by the action of methylic iodide on ethylic thioncarbamate. This is explained by assuming that in both reactions an intermediate additive compound is formed; in the case of ethylic thioncarbamate,  $\text{NH}_2\cdot\text{CS}\cdot\text{OEt}$ , this would have either the structure  $\text{NH}_2\cdot\text{C}(\text{OEt})\cdot\text{SMel}$ , assuming sulphur to be quadrivalent, or  $\text{NH}_2\cdot\text{C}(\text{OEt})\cdot\text{I}\cdot\text{SMe}$ , assuming it to be bivalent, and, by the loss of ethylic iodide, would give rise to methylic thiolcarbamate,  $\text{NH}_2\cdot\text{CO}\cdot\text{SMe}$ .

When ethylic thioncarbamate is left in contact with ethylic iodide, it yields ethylic thiolcarbamate ("carbonylsulphethylamine," Conrad and Salomon, *Abstr.*, 1875, 753), which melts at  $107\text{--}108^\circ$ .

Isoamylic thioncarbamate, in contact with isopropyl iodide, gives rise to *isopropyl thiolcarbamate*,  $\text{NH}_2\cdot\text{CO}\cdot\text{SPr}^i$ , which crystallises from water in colourless, rectangular plates, and melts at about  $125^\circ$ .

\* The authors adopt the Geneva nomenclature, *thion* being used to denote compounds containing the group  $\cdot\text{CS}\cdot\text{OR}$ , and *thiol* those containing the group  $\cdot\text{CO}\cdot\text{SR}$ .

Isobutylic thioncarbamate,  $\text{NH}_2 \cdot \text{CS} \cdot \text{O} \cdot \text{C}_4\text{H}_9$ , prepared by the action of alcoholic ammonia on isoamylic ethyldithiocarbonate,  $\text{SEt} \cdot \text{CS} \cdot \text{O} \cdot \text{C}_5\text{H}_{11}$ , crystallises from ether or water in white plates and melts at  $51-53^\circ$ , not at  $36^\circ$  (Mylius, *Ber.*, 1872, 5, 976), or  $10^\circ$  (Blankenhorn, *loc. cit.*): with dilute alcoholic silver nitrate, it produces a white precipitate which turns black; with mercuric chloride, a permanently white precipitate; with copper sulphate, a white precipitate which becomes black on warming, and with platinic chloride, a yellow precipitate which, when warmed, decomposes. *Isobutylic thiolcarbamate*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{C}_4\text{H}_9$ , prepared by heating it with isobutylic iodide at  $120^\circ$  for several hours, crystallises from water in thin, snow-white plates and melts at  $102-103^\circ$ ; with both silver nitrate and mercuric chloride, it forms a white precipitate which does not blacken, but with copper sulphate and platinic chloride, no precipitate is produced.

Isoamylic thioncarbamate (Johnson, this Journal, 1853, 5, 142), when heated with isoamylic iodide, yields the corresponding thiolcarbamate,  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{C}_5\text{H}_{11}$ , melting at  $112-113^\circ$ , not at  $107^\circ$  (Schöne, *Abstr.*, 1886, 337).

When ethylenic bromide is heated with ethylic thioncarbamate for 3 hours at  $100^\circ$ , the *ethylene* derivative,  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{CO} \cdot \text{NH}_2$ , of thiolcarbamic acid is obtained as a crystalline powder, together with small quantities of ethylic thiolcarbamate; the compound  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$  is not formed.

In the light of these results, the fact observed by Debus (*Annalen*, 1849, 72, 18), that ethylic thioncarbamate, when heated, gives rise to ethyl mercaptan and cyanuric acid, is explained; it is probable that, in the first instance, the isomeric thiolcarbamate is formed by molecular rearrangement. The authors discuss the structure of the ammonium thiocarbamate, formed by the action of ammonia on carbon oxy-sulphide, and point out that the argument for Fleischer's formula,  $\text{NH}_2 \cdot \text{CO} \cdot \text{SNH}_4$  (*Ber.*, 1876, 9, 991), based on the fact that ethylic thiolcarbamate is formed when the compound is heated with ethylic bromide at  $100^\circ$ , does not preclude the thion structure; moreover, the ease with which the salt is desulphurated points to its being  $\text{NH}_2 \cdot \text{CS} \cdot \text{ONH}_4$ , for the analogous compound,  $\text{NH}_2 \cdot \text{CS} \cdot \text{OEt}$ , is readily desulphurated by silver nitrate, whilst the compound  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{C}_7\text{H}_7$  yields a stable silver salt. W. A. D.

**Benzoylfurfuran.** By R. MARQUIS (*Compt. rend.*, 1899, 129, 111-113).—*Benzoylfurfuran*,  $\text{C}_4\text{OH}_3 \cdot \text{CO} \cdot \text{Ph}$ , obtained by the action of pyromucic chloride on benzene in the presence of aluminium chloride, is a colourless liquid which boils at  $185^\circ$  under 43 mm. pressure, does not solidify at  $-15^\circ$ , and has a sp. gr. 1.183 at  $19^\circ$ . On oxidation with potassium permanganate, it gives benzoic acid and another acid melting at  $52^\circ$ , which has not yet been further studied. The *oxime* forms fine, yellow needles, is very soluble in organic solvents, melts at  $132^\circ$ , and is decomposed at a slightly higher temperature; with acetic anhydride, it gives two *acetyl* derivatives melting at  $68^\circ$  and  $109^\circ$  respectively. *Phenylfurfurylamine*,  $\text{C}_4\text{OH}_3 \cdot \text{CHPh} \cdot \text{NH}_2$ , prepared by reduction of an alcoholic solution of the oxime with metallic sodium, is a colourless liquid which has a faint odour, becomes brown



even in the dark, and loses ammonia spontaneously. It boils at  $167\text{--}168^\circ$  under 43—44 mm. pressure. The *acetyl* derivative melts at  $127^\circ$ . The *hydrochloride* forms extremely soluble, small prisms. The *platinochloride*,  $(C_{11}H_{11}NO)_2, H_2PtCl_6 + 2H_2O$ , crystallises in small, golden plates easily soluble in hot, but only slightly so in cold water; it decomposes at  $100^\circ$ .  
H. R. LE S.

**Methylpentamethylene and its Derivatives.** By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1899, 307, 335—367. Compare Abstr., 1898, i, 637).—Methylpentamethylene (methylcyclopentane) is a limpid liquid having the odour of light petroleum; it boils at  $71\text{--}72^\circ$  under 759 mm. pressure, does not solidify at  $-79^\circ$ , and has a sp. gr. 0.76406 at  $0^\circ/0^\circ$  and 0.7430 at  $20^\circ/0^\circ$  (compare Abstr., 1897, i, 401). Fuming nitric acid of sp. gr. 1.55 acts but slowly on the hydrocarbon if the mixture is kept cold, but above  $0^\circ$  action takes place with great violence; a mixture of nitric and sulphuric acids, however, is almost without action. Methylpentamethylene and its homologues are not alone in their activity towards nitric acid, which also attacks the substituted hexamethylenes.

1:3-Methylketopentamethylene (1:3-Methylcyclopentanone), the ketone obtained by distilling the calcium salt of  $\beta$ -methyladipic acid, yields the *oxime* in two modifications, which crystallise in needles, and melt at  $67\text{--}69^\circ$  and  $87\text{--}89.5^\circ$  respectively (compare Semmler, Abstr., 1893, i, 130).

3:1-Amidomethylpentamethylene,  $\begin{array}{c} CHMe-CH_2 \\ | \\ CH_2 \cdot CH(NH_2) \end{array} > CH_2$ , prepared by reducing the oxime in alcoholic solution with sodium, has a powerful ammoniacal odour, and mixes with water in all proportions; it boils at  $124^\circ$  under 754 mm. pressure, and has a sp. gr. 0.8594 at  $0^\circ/0^\circ$ , 0.8422 at  $20^\circ/0^\circ$ , and 0.8429 at  $20^\circ/20^\circ$ . The *hydrochloride* dissolves readily in water and is optically inactive, whilst the *platinochloride* crystallises in orange leaflets; the *benzoyl* derivative separates from dilute alcohol in slender needles and melts at  $115\text{--}117^\circ$ .

3:1-Hydroxymethylpentamethylene (1:3-Methylpentamethylenol),  $\begin{array}{c} CHMe-CH_2 \\ | \\ CH_2 \cdot CH(OH) \end{array} > CH_2$ , obtained on reducing the ketone in moist ether with sodium, boils at  $150\text{--}151^\circ$  (uncorr.). The secondary *iodide*, prepared by heating the alcohol with hydriodic acid, iodine, and red phosphorus at  $100^\circ$  during 8 hours, boils at  $177\text{--}179^\circ$  with slight decomposition.

1:1-Nitromethylpentamethylene,  $\begin{array}{c} CMe(NO_2) \cdot CH_2 \\ | \\ CH_2 - CH_2 \end{array} > CH_2$ , a colourless liquid having the odour of turpentine and camphor, boils at  $92^\circ$  under 40 mm. pressure without decomposition, but under 750 mm. pressure it decomposes, and the boiling point rises from  $177^\circ$  to  $184^\circ$ . Its sp. gr. is 1.0568 at  $0^\circ/0^\circ$ , 1.0400 at  $20^\circ/0^\circ$ , and 1.0453 at  $15^\circ/15^\circ$ .

1:1-Amidomethylpentamethylene,  $\begin{array}{c} CMe(NH_2) \cdot CH_2 \\ | \\ CH_2 - CH_2 \end{array} > CH_2$ , obtained by reducing the nitro-compound with tin and hydrochloric acid, is an ammoniacal liquid which fumes in air and dissolves readily

in water; it boils at  $114^{\circ}$  under 753 mm., and has a sp. gr. 0.8367 at  $0^{\circ}/0^{\circ}$ , and 0.8197 at  $20^{\circ}/0^{\circ}$ . The *hydrochloride* melts above  $240^{\circ}$ , and the *hydrobromide* crystallises in long needles; the *platinochloride*,  $(C_6H_{13}N)_2, H_2PtCl_6 + H_2O$ , forms orange-red octahedra, darkens at  $205^{\circ}$ , and decomposes at  $220^{\circ}$ . The *aurichloride* crystallises in very long, orange-yellow needles, and decomposes at  $172-174^{\circ}$ ; the *auribromide* forms black leaflets.

1:1-Methylpentamethylenol,  $\begin{array}{c} CMe(OH) \cdot CH_2 \\ | \\ CH_2 - CH_2 \end{array} > CH_2$ , formed from the amine by the action of nitrous acid, solidifies in long, transparent needles at  $32^{\circ}$ , and boils at  $135-136^{\circ}$ , when it decomposes in part. Fuming hydrochloric acid converts it into the *chloride*, which boils at  $97^{\circ}$  and  $122-123^{\circ}$  under pressures of 349 mm. and 757 mm. respectively, in part decomposing at the higher temperature, yielding a hydrocarbon,  $C_6H_{10}$ , and hydrogen chloride.

Methylcyclopentene-1:2,  $\begin{array}{c} CMe \cdot CH_2 \\ | \\ CH - CH_2 \end{array} > CH_2$ , a bye-product in the preparation of the alcohol, boils at  $72^{\circ}$  under 754 mm. pressure; when mixed with 6 parts of slightly fuming hydrochloric acid, the temperature rises to  $28^{\circ}$ , and after 15 minutes interval the hydrocarbon becomes green, and the acid, black.

The 2-chloride,  $\begin{array}{c} CH_2Me \cdot CH_2 \\ | \\ CHCl - CH_2 \end{array} > CH_2$ , boils at  $126^{\circ}$ , and has a sp. gr. 0.9281 at  $0^{\circ}/0^{\circ}$ , the *hydrocarbon*,  $C_6H_{10}$ , obtained from it by reduction, boils at  $69-70^{\circ}$  under 756 mm. pressure, and has a sp. gr. 0.7352 at  $0^{\circ}/0^{\circ}$ .

2:1-Nitromethylpentamethylene,  $\begin{array}{c} CHMe - CH_2 \\ | \\ CH(NO_2) \cdot CH_2 \end{array} > CH_2$ , boils at  $185-186^{\circ}$  under 758 mm. pressure, when it decomposes; its sp. gr. is 1.0462 at  $0^{\circ}/0^{\circ}$  and 1.0296 at  $20^{\circ}/0^{\circ}$ .

2:1-Amidomethylpentamethylene,  $\begin{array}{c} CHMe - CH_2 \\ | \\ CH(NH_2) \cdot CH_2 \end{array} > CH_2$ , boils at  $121-122^{\circ}$  under 738 mm. pressure; its sp. gr. is 0.8179 at  $0^{\circ}/0^{\circ}$  and 0.8006 at  $20^{\circ}/0^{\circ}$ . The *hydrochloride* crystallises in small needles, and the *platinochloride*,  $(C_6H_{13}N)_2, H_2PtCl_6$ , begins to decompose at  $240^{\circ}$ ; the *aurichloride* crystallises in lustrous, pale yellow leaflets, with  $1H_2O$ , and at  $100^{\circ}$  dissolves in its water of crystallisation.

M. O. F.

Structure of the so-called Hexanaphthenecarboxylic Acid. By WLADIMIR B. MARKOWNIKOFF (*Annalen*, 1899, 307, 367-374).—The existence of pentamethylene derivatives in Caucasian naphtha suggested the identity of Aschan's hexanaphthenecarboxylic acid with methylpentamethylenecarboxylic acid,  $\begin{array}{c} CH_2 \cdot CHMe \\ | \\ CH_2 - CH_2 \end{array} > CH \cdot COOH$ . This is now shown to be the case by converting the methylic salt into the amide, and the latter into the amine, which is found to be identical with 2:1-amidomethylpentamethylene, described in the foregoing abstract.

M. O. F.

**Isomerisation in the Synthesis of Aromatic Hydrocarbons by Friedel's Reaction.** III. Synthesis of Amylbenzene and its Derivatives. By MICHAEL KONOWALOFF and J. EGOROFF (*Chem. Centr.*, 1899, i, 776—777; from *J. Russ. Chem. Soc.*, 1898, 30, 1031—1035. Compare *J. Russ. Chem. Soc.*, 26, 202; 27, 456).—By the action of isoamylic chloride on benzene in presence of aluminium chloride, amylbenzene is formed. This compound boils at 187—189° under 755 mm. pressure, and by the action of nitric acid at 105° yields secondary nitroamylbenzene and tertiary nitrophenylmethylisopropylmethane. The former compound is obtained in solution by distilling off the unchanged hydrocarbon and then treating with sodium ethoxide and afterwards with water, whilst the latter remains undissolved.

*Secondary nitroamylbenzene*,  $\text{NO}_2 \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , boils at 159—161° under 20 mm. pressure, has a sp. gr. 1.08991 at 0°/0°, 1.07362 at 20°/0°, and a specific refractive index  $[n]_D$  1.53140 at 20°; it gives the pseudonitrol reaction with nitrous acid and is oxidised to benzoic acid by potassium permanganate. The *amine*, prepared by reducing the nitro-compound with tin and hydrochloric acid, boils at 232—235° under 756 mm. pressure, forms crystalline salts, and absorbs carbonic anhydride with avidity.

*Tertiary nitrophenylmethylisopropylmethane*,  $\text{NO}_2 \cdot \text{CMePh} \cdot \text{CHMe}_2$ , boils at 151—153° under 20 mm. pressure, has a sp. gr. 1.09414 at 0°/0°, 1.07825 at 20°/0°, and a specific refractive index  $[n]_D$  1.520402 at 20°. The *amine* boils at 226—227° under 739 mm. pressure, has a sp. gr. 0.95239 at 0°/0°, 0.93482 at 20°/0°, specific refractive index  $[n]_D$  1.51781 at 20°, and forms crystalline salts; when oxidised by potassium permanganate, the hydrochloride forms benzoic acid.

Besides isoamylbenzene and phenylmethylisopropylmethane, the product of the original reaction contains a hydrocarbon which is not attacked even by repeatedly treating with nitric acid. This compound is probably phenyldimethylethylmethane,  $\text{CMe}_2\text{Ph} \cdot \text{CH}_2\text{Me}$ ; it boils at 189—191° and has sp. gr. 0.8889 at 0°/0° and 0.8740 at 20°/0°.

The following conclusions are deduced from these results. (1) Isoamylic chloride, when treated with benzene by Friedel's reaction, is not completely converted into isomerides either at a low temperature or at the boiling point of benzene. (2) Two types of isomerides are formed, the isoamyl radicle,  $\cdot\text{CH}_2 \cdot \text{CH} \cdot \text{CHMe}_2$ , becoming either  $\cdot\text{CHMe} \cdot \text{CHMe}_2$  or  $\cdot\text{CEtMe}_2$ .

E. W. W.

**Isomerisation in the Synthesis of Aromatic Hydrocarbons by Friedel's Reaction.** IV. Isomerisation of the Isobutyl Radicle. By MICHAEL KONOWALOFF (*Chem. Centr.*, 1899, i, 777; from *J. Russ. Chem. Soc.*, 1898, 30, 1036—1040. Compare preceding abstract).—The product of the action of isobutylic chloride on toluene in presence of aluminium chloride boils at 188—188.5° and when treated with nitric acid forms the *nitro*-derivatives,  $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}_3$  [ $\text{CH}_2 : \text{CMe}_3 = 1 : 3$  and  $1 : 4$ ], of the corresponding methyl-tertiary-butylbenzenes. The potassium salts obtained from this mixture, when oxidised by potassium permanganate, yield terephthalic, meta-butylbenzoic, and parabutylbenzoic acids, and give the nitrolic acid reaction. In this case, therefore, the isobutyl radicle,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot$ ,

has been completely converted into the tertiary butyl radicle,  $\cdot\text{CMe}_3$ , the methyl group of the toluene having no influence on the extent of the isomerisation of the radicle united to the halogen. The formation of butylbenzoic acids is opposed to the rule that the longer side chain is oxidised to carboxyl; this oxidation of the longer chain, however, is really due, not to its length, but to its containing  $\text{CH}_2$ - or  $\text{CH}$ -groups attached directly to the benzene ring, such groups being more easily oxidised than methyl groups. In this case, however, the longer side chain has no such groups and the methyl is therefore attacked.

E. W. W.

**Phenylic Chlorocarbonates.** By ETIENNE BARRAL and ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 727—728. Compare this vol., i, 747).—*Phenylic chlorocarbonate*,  $\text{COCl}\cdot\text{OPh}$ , is a colourless liquid which rapidly becomes red; it boils without decomposition at  $95^\circ$  under 20 mm. and at  $97$ — $98^\circ$  under 25 mm. pressure, but under the ordinary pressure it boils at  $187^\circ$ , decomposing into phosgene and diphenylic carbonate. *Orthotolylic chlorocarbonate*,  $\text{COCl}\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{Me}$ , is a colourless liquid which rapidly becomes violet; it boils at  $119^\circ$  under 35 mm. at  $114^\circ$  under 25 mm. pressure, and when boiled under the ordinary pressure decomposes into phosgene and di-orthotolylic carbonate. *Guaiacylic chlorocarbonate*,  $\text{COCl}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , boils at  $112^\circ$  under 25 mm. pressure, but decomposes when boiled under the ordinary pressure, yielding diguaiacylic carbonate. *Thymylic chlorocarbonate*,  $\text{COCl}\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{MePr}$ , boils at  $122$ — $124^\circ$  under 25 mm. pressure, and when boiled under ordinary conditions yields dithymylic carbonate.

W. A. D.

[**Derivatives of Ethoxyphenol.**] By EMANUEL MERCK (*Chem. Centr.*, 1899, i, 706; from *Jahresber.*, 1898, 25—142).—*Ethoxyphenylic benzoate*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$  [ $\text{OEt}:\text{OBz}=1:2$ ] forms colourless crystals, melts at  $31^\circ$ , and is easily soluble in alcohol or ether; the *salicylate*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , forms colourless crystals, melts at  $40$ — $41^\circ$ , and is soluble in alcohol or ether; the *butyrate*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{COPr}$ , is a colourless liquid, boils at  $260^\circ$ , and is miscible with alcohol or ether; the *valerate*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{C}_4\text{H}_9$ , is a colourless liquid, boils at  $262^\circ$ , and is miscible with alcohol, ether, or chloroform; the *phosphate*,  $(\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3\text{PO}$ , forms colourless crystals, melts at  $131$ — $132^\circ$ , and is soluble in alcohol.

E. W. W.

**Egols. New Antiseptics.** By E. GAUTRELET (*Compt. rend.*, 1899, 129, 113—114).—Orthonitro-phenol-, cresol-, or thymol-parasulphonic acid easily absorbs half an atomic proportion of mercury. To the resulting parasulphonates of mercury and potassium, the generic name of *egol* is given, each compound being distinguished by a prefix indicating the phenol from which it is derived, thus: *phenegol*, *cresegol*, *thymegol*. The egols are very stable compounds, from which mercury can be separated only by heating with soda-lime or by treating with potassium chlorate and hydrochloric acid. They form red-brown powders, are difficult to crystallise, and dissolve in water, but not in strong alcohol. The aqueous solutions are odourless, neutral, and

non-irritant, do not coagulate albumins, are not decomposed by organic substances, and precipitate the toxins. They are not toxic, as, when introduced hypodermically, 2 grams per kilo. of the weight of the animal are required to cause death, but are powerful bactericides, 4 grams per 1000 introduced into a culture preventing all bacterial growth.

H. R. LE S.

**Condensation of Succinic Anhydride and Pyrogallol.** By GEORG VON GEORGIEVICS (*Monatsh.*, 1899, 20, 450—461).—The author has isolated two dyes from the numerous substances which are formed by the condensation of succinic anhydride and pyrogallol.

*Pyrogallolsuccinein*,  $C_{16}H_{14}O_8$ , is obtained when a mixture of equal parts of succinic anhydride and zinc chloride is heated for several hours at  $170^\circ$  with an equal weight of pyrogallol. It forms a reddish-brown powder, is practically insoluble in the ordinary solvents, and decomposes at  $180^\circ$ . When boiled with alcoholic hydrochloric acid, it yields a *monohydrochloride* crystallising in brownish-yellow, microscopic plates. The *sulphate* crystallises from concentrated sulphuric acid in dark-blue crystals. The colouring properties of pyrogallol-succinein are very similar to those of gallein.

*Digallacyl*,  $C_6H_2(OH)_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot C_6H_2(OH)_3$ , is prepared by heating a fused mixture of 1 part of succinic anhydride and 2 parts of pyrogallol for 10 minutes at  $150^\circ$  with one-third its weight of zinc chloride. It crystallises in tufts of slender, glistening, colourless needles, and darkens, without fusing, at about  $270^\circ$ . It dissolves in alcohol or acetic acid, but is almost insoluble in other ordinary solvents; strong caustic soda dissolves it, forming a yellow solution, whilst in cold concentrated sulphuric acid it forms a yellow solution which, when warmed, suddenly becomes a deep violet. As a dye, it is very similar to gallacetophenone. *Hexacetyldigallacyl* forms microscopic prisms, melts at  $170$ — $171^\circ$ , and is very soluble in acetic acid, but almost insoluble in alcohol. *Digallacylosazone* crystallises from alcohol with 1 mol. of the solvent in tufts of yellowish needles, darkens in colour about  $190^\circ$ , and decomposes suddenly at  $206$ — $207^\circ$ .

R. H. P.

**Isomeric Change in [the Formation of] Homologues of Phloroglucinol.** By R. REISCH (*Monatsh.*, 1899, 20, 488—503).—Various homologues of phloroglucinol, in methyl alcoholic solution, were treated successively with sodium methoxide and methylic iodide. Trimethylphloroglucinol gave a quantitative yield of hexamethylphloroglucinol: dimethylphloroglucinol a mixture of hexamethyl- and tetramethyl-phloroglucinol: monomethylphloroglucinol, a mixture of hexamethyl-, pentamethyl-, and tetramethyl-phloroglucinol: products exclusively of the ketonic type. Trimethylphloroglucinol monomethylic ether yielded pentamethylphloroglucinol monomethylic ether; dimethylphloroglucinol gave a product soluble in alkali, probably tetramethylphloroglucinol, together with tetra- and probably penta-methylphloroglucinol monomethylic ether; monomethylphloroglucinol monomethylic ether gave a mixture of tetra- and penta-methylphloroglucinol monomethylic ethers: no increase in the number of methoxyl groups occurs, ketonic compounds being formed as the result of methylation.

*Tetramethylphloroglucinol monomethylic ether*,  $C_6HMe_4O_2 \cdot OMe$ , crystallises in colourless, glistening plates [ $a : b : c = 0.7039$ ;  $\xi = 92^\circ 1'$ ;  $\eta = 79^\circ 6'$ ;  $\zeta = 98^\circ 6'$ ], melts at  $63^\circ$ , boils at  $143^\circ$  under 16 mm. pressure, dissolves very readily in alcohol, benzene, or ethylic acetate, but less readily in light petroleum, and is insoluble in water. The *pentamethyl* derivative is a yellowish, thick liquid and boils at  $139^\circ$  under 19 mm. pressure.

R. H. P.

**Filicic Acid.** By RUDOLF BOEHM (*Annalen*, 1899, 307, 249—282. Compare Abstr., 1898, i, 40, and this vol., i, 32).—The author represents the constitution of filicic acid by one of the formulæ  $CMe_2 \begin{smallmatrix} \diagup C(OH):CH \\ \diagdown C(OH):CH \end{smallmatrix} CO$ , and  $CMe_2 \begin{smallmatrix} \diagup C(OH):CH \\ \diagdown CO-CH \end{smallmatrix} \gg C \cdot OH$ , which illustrate the close relation between this compound and phloroglucinol; tetrabromofilicic acid has the constitution expressed by the formula  $CMe_2 \begin{smallmatrix} \diagup CO \cdot CBr_2 \\ \diagdown CO \cdot CBr_2 \end{smallmatrix} CO$ .

Filicic acid crystallises from alcohol in small, colourless cubes, and melts at  $213\text{--}215^\circ$ , when it becomes brown; the aqueous solution develops a red coloration with ferric chloride, and reduces potassium permanganate and an ammoniacal silver solution. On adding a colourless specimen of aniline to the alcoholic solution, a beautiful, reddish-violet coloration is slowly developed; when the crystalline acid is heated with aniline and acetic anhydride or glacial acetic acid, an emerald green coloration is gradually produced. The *methyl ether*,  $C_8H_9O_2 \cdot OMe$ , prepared by saturating a hot solution of filicic acid in methylic alcohol with hydrogen chloride, crystallises from ethylic acetate in colourless, lustrous prisms, and melts at  $208^\circ$ ; it dissolves with difficulty in boiling water, and develops a violet red coloration with ferric chloride. The *ethyl ether* crystallises from alcohol in lustrous prisms, and melts at  $215^\circ$ ; the *diethyl ether*,  $C_8H_8O(OEt)_2$ , prepared by heating it with ethylic iodide and alcoholic potash, crystallises from light petroleum in quadratic plates or long prisms melting at  $103\text{--}105^\circ$ , and is indifferent towards ferric chloride. The *diacetyl* derivative,  $C_8H_8O(OAc)_2$ , crystallises from alcohol in large, six-sided plates and melts at  $82\text{--}85^\circ$ ; it is indifferent towards ferric chloride. When the potassium salt of filicic acid is oxidised with potassium permanganate, 35 per cent. of dimethylmalonic acid is produced.

The *dichloride* of filicic acid,  $C_8H_8Cl_2O$ , prepared by the action of phosphorus pentachloride, crystallises from light petroleum in six-sided and rhombic plates, melting at  $79\text{--}80^\circ$ . The *compound*,  $C_8H_9O_2 \cdot O \cdot POCl_2$ , arising from the action of phosphorus oxychloride, occurs as a bye-product; it crystallises from chloroform in small plates, and decomposes at  $158\text{--}160^\circ$ .

*Dibromofilicic acid*,  $C_8H_8Br_2O_3$ , prepared by suspending filicic acid in absolute alcohol and slowly adding bromine, crystallises from carbon bisulphide in large, colourless prisms, and melts at  $147\text{--}148^\circ$ ; exposure to air causes the substance to become yellow, and change gradually into bromofilicic acid, which is also produced when the

dibromo-compound is digested with glacial acetic acid or with boiling water.

*Tribromofilicic acid*,  $C_8H_7Br_3O_3$ , obtained when bromine acts on filicic acid in the dry state or suspended in glacial acetic acid, crystallises from carbon bisulphide in lustrous, rhombic plates and prisms, becoming yellow at  $120^\circ$  and melting at  $132^\circ$ .

*Bromofilicic acid*,  $C_8H_9BrO_3$  or  $C_8H_7BrO_3$ , produced when either of the foregoing bromo-compounds is digested with boiling water, dissolves with difficulty in common solvents excepting acetone; it crystallises from glacial acetic acid in small, orange-red cubes and quadratic plates, and decomposes without fusion above  $250^\circ$ . Filicic acid is regenerated when the bromo-derivative is reduced with sodium amalgam, and oxidation with potassium permanganate gives rise to dimethylmalonic acid.

*Tetrabromofilicic acid* (*dimethyltetrabromocyclohexane-1:3:5-trione*),  $C_8H_6Br_4O_3$ , formed when tribromofilicic acid is dissolved in excess of bromine, is best prepared by slowly adding bromine to a neutral or feebly alkaline solution of filicic acid in aqueous potash; it crystallises from alcohol in lustrous prisms and six-sided plates, melting at  $139^\circ$ . The alcoholic solution is indifferent towards ferric chloride, but liberates iodine from potassium iodide. Caustic alkalis act readily on tetrabromofilicic acid, converting it into hexabromodimethylacetylacetone, and the compound,  $C_7H_7BrO_3$ , which crystallises from water in colourless, lustrous prisms containing  $1\frac{1}{2}H_2O$ , melts at  $179-180^\circ$  when anhydrous, develops an intense red coloration with ferric chloride and yields a crystalline *barium* salt.

*Hexabromodimethylacetylacetone*,  $CMe_2(CO\cdot CBr_3)_2$ , is prepared by adding finely powdered filicic acid to a large excess of bromine, and, after an interval, adding 15 per cent. caustic soda until the liquid is alkaline; it separates from glacial acetic acid in large, lustrous crystals, and melts at  $149-150^\circ$ . The alcoholic solution is indifferent towards ferric chloride, and liberates iodine from potassium iodide.

*Tetrabromodimethylacetylacetone*,  $C_7H_8Br_4O_2$ , obtained by adding bromine to dimethylacetylacetone until action ceases and allowing the excess of halogen to evaporate, crystallises from light petroleum in large, lustrous prisms and melts at  $78^\circ$ ; further treatment with bromine leaves the substance unchanged, but if a solution in the halogen is treated with 15 per cent. caustic soda, hexabromodimethylacetylacetone is produced.

*Tetrachlorofilicic acid*,  $C_8H_6Cl_4O_3$ , prepared by saturating with chlorine a solution of filicic acid in chloroform, crystallises in snow-white prisms several centimetres in length; it melts at  $83-84^\circ$ .

*Symmetrical tetrachlorodimethylacetylacetone*,  $CMe_2(CO\cdot CHCl_2)_2$ , formed from tetrachlorofilicic acid by the action of water, crystallises from light petroleum in large, lustrous prisms, and melts at  $95-96^\circ$ .

M. O. F.

**Optical Activity of Tannin.** By FLAVIAN FLAWITZKY (*Chem. Centr.*, 1899, i, 327; from *J. Russ. Chem. Soc.*, 1898, 30, 748-749).—A remark of Walden (*Ber.*, 1897, 30, 3151) makes the author call attention to the fact that he was the first to determine the optical

activity of tannin (*J. Russ. Chem. Soc.*, **22**, 362). The specific rotation of tannin for sodium and lithium light is as follows:  $[\alpha]_D^{25} + 50.3^\circ$  for  $c = 13.11$  in water,  $[\alpha]_D^{25} 58^\circ$  for same solution decolorised by animal charcoal;  $[\alpha]_D^{25} 22^\circ$  and  $[\alpha]_D^{25} 17.4^\circ$  for  $c = 4.596$  in ethylic alcohol;  $[\alpha]_D^{25} 24.5^\circ$  and  $[\alpha]_D^{25} 19.4^\circ$  for  $c = 11.576$  in acetic acid. J. C. P.

**Action of Paranitrobenzylic Chloride on Dimethylaniline and on Diphenylamine.** By EDGAR WEDEKIND [and J. GONSWA] (*Annalen*, 1899, **307**, 283—293).—*Phenylparanitrobenzyldimethylammonium chloride*,  $C_{15}H_{17}N_2O_2Cl$ , produced when a mixture of dimethylaniline and paranitrobenzylic chloride is left at the ordinary temperature for some months, crystallises from alcohol in four-sided plates belonging to the monoclinic system  $[a:b:c = 1.3317:1:1.7511]$ ; it melts at  $118\text{--}120^\circ$ , and yields salts with gold and platinum chlorides.

If the foregoing mixture is heated until ebullition begins, vigorous action takes place, and methyl-violet is formed, along with *paranitrotetramethyldiamidotriphenylcarbinol*,  $C_{23}H_{25}N_3O_3$ , a pale yellow, crystalline substance, which sinters at  $80^\circ$ , and melts indefinitely at  $100\text{--}105^\circ$ ; the *picrate* is a deep green powder melting to a brownish mass below  $100^\circ$ .

When paranitrobenzylic chloride is heated with diphenylamine until action takes place, diphenylamine-blue is obtained; the nature of the bye-product has not been yet determined. M. O. F.

**Action of Aromatic Amines on Chloracetylurethanes and Chloracetocarbamides.** By G. FRERICHs and HEINRICH BECKURTS (*Arch. Pharm.*, 1899, **237**, 331—346).—When a chloracetocarbamide,  $NHR^1 \cdot CO \cdot NH \cdot CO \cdot CH_2Cl$  (1 mol.), is heated on the water-bath with an amine,  $NHR^{11} \cdot C_6H_4R^{111}$  (rather more than 2 mols.), the product is a glycocinylcarbamide,  $NHR^1 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot NR^{11} \cdot C_6H_4R^{111}$  [ $R^1$ ,  $R^{11}$ ,  $R^{111}$  may each be H]. The following were obtained; the numbers given are their melting points, and  $R^1$ ,  $R^{11}$ , and  $R^{111}$  are to be understood as H where the contrary is not indicated. *Phenyl-glycocinylcarbamide*,  $176^\circ$ ; *2-tolyl-* [ $R^{111} = Me$ ],  $196^\circ$ ; *4-tolyl-*,  $178^\circ$ ; *4-ethoxyphenyl-* [ $R^{111} = OEt$ ],  $177^\circ$ ; *methylphenyl-* [ $R^{11} = Me$ ],  $200^\circ$ ; *ethylphenyl-* [ $R^{11} = Et$ ],  $200^\circ$ . *Phenyl-glycocinyl-methyl-carbamide* [ $R^1 = Me$ ],  $145^\circ$ ; *4-ethoxyphenyl-methyl-* [ $R^{111} = OEt$ ,  $R^1 = Me$ ],  $170^\circ$ ; *phenyl-phenyl-* [ $R^1 = Ph$ ],  $160^\circ$ ; *2-tolyl-phenyl-* [ $R^{111} = Me$ ,  $R^1 = Ph$ ],  $175^\circ$ ; *4-tolyl-phenyl-*,  $176^\circ$ ; *4-ethoxyphenyl-phenyl-* [ $R^{111} = OEt$ ,  $R^1 = Ph$ ],  $154^\circ$ ; *phenyl-4-ethoxyphenyl-* [ $R^1 = C_6H_4 \cdot OEt$ ],  $162^\circ$ ; *2-tolyl-4-ethoxyphenyl-* [ $R^{111} = Me$ ,  $R^1 = C_6H_4 \cdot OEt$ ],  $183^\circ$ ; *4-tolyl-4-ethoxyphenyl-*,  $172^\circ$ ; *4-ethoxyphenyl-4-ethoxyphenyl-* [ $R^{111} = C_6H_4 \cdot OEt$ ,  $R^1 = OEt$ ],  $162^\circ$ . Such of these glycocinylcarbamides as have  $R^{11} = H$  lose ammonia or a substituted amine when heated to a high temperature, and yield  $\beta$ -hydantoins,  $CO \begin{smallmatrix} \diagup N(C_6H_4R^{111}) \cdot CH_2 \\ \diagdown NH \end{smallmatrix} \text{---} CO$  (see below). These are also the

direct products when the chloracetocarbamide is heated with the amine to a high temperature.

When a chloracetylurethane,  $COOR \cdot NH \cdot CO \cdot CH_2Cl$ , is heated at not too high a temperature, and for not too long a time, with an



amine,  $\text{NHR}^{11} \cdot \text{C}_6\text{H}_4\text{R}^{11}$ , preferably with the addition of a little alcohol, a glycocinylurethane,  $\text{COOR} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NR}^{11} \cdot \text{C}_6\text{H}_4\text{R}^{11}$ , is formed. *Phenyl-glycocinyl-ethyl-urethane* [ $\text{R} = \text{Et}$ ],  $80^\circ$ ; *2-tolyl-ethyl-* [ $\text{R}^{11} = \text{Me}$ ,  $\text{R} = \text{Et}$ ],  $120^\circ$ ; *4-tolyl-ethyl-*,  $90-100^\circ$ ; *4-ethoxyphenyl-ethyl* [ $\text{R}^{11} = \text{OEt}$ ,  $\text{R} = \text{Et}$ ],  $100^\circ$ ; *methylphenyl-ethyl-* [ $\text{R}^{11} = \text{Me}$ ,  $\text{R} = \text{Et}$ ],  $117^\circ$ ; *Methylphenyl-isobutyl-* [ $\text{R}^{11} = \text{Me}$ ,  $\text{R} = \text{iso-Bu}$ ],  $103^\circ$ . Such of these compounds as have  $\text{R}^{11} = \text{H}$  have a certain basic character, being very soluble in dilute acids; they also decompose when they melt. Moreover, they readily lose alcohol when heated alone or with caustic soda, forming  $\beta$ -hydantoins (see above); and in fact these are the products obtained directly when the chloracetylurethane is heated with the amine for some time on the water-bath.  *$\beta$ -4-Ethoxyphenyl-hydantoin* [ $\text{R}^{11} = \text{OEt}$ ], melting at  $234^\circ$ , appears to be a new compound. These hydantoins are also formed when the substituted chloracetylphenylcarbamides are heated with alcoholic potash. With alkalis, they yield salts of the corresponding hydantoic acids; *potassium 4-ethoxyphenylhydantoate*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{N}(\text{C}_6\text{H}_4 \cdot \text{OEt}) \cdot \text{CH}_2 \cdot \text{COOK}$ , was analysed.

C. F. B.

**Combination of Phenylhydrazine with Sodium Hydrogen Sulphite.** By PASTUREAU (*J. Pharm.*, 1899, [vi], 9, 574—575. Compare this vol., i, 205). The precipitate formed when phenylhydrazine is added to a sodium hydrogen sulphite solution appears to have the composition  $\text{NaHSO}_3 \cdot 2\text{N}_2\text{H}_3\text{Ph}$ . It is very soluble in water, crystallises in colourless needles radiating from a centre, and decomposes when heated to  $100^\circ$ .

H. R. LE S.

**Compounds of Phenylhydrazine with Cuprous Salts.** By JOSEPH MOITESSIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 666—668).—The compounds which phenylhydrazine forms with cuprous chloride, bromide, and iodide are nearly insoluble in cold water, dissolve in sodium thiosulphate solution, and are decomposed by alcohol and ether, which dissolve out the phenylhydrazine. They gradually alter on exposure to air, especially when moist, and are rapidly decomposed at higher temperatures. *Phenylhydrazine cuprochloride*,  $2\text{Cu}_2\text{Cl}_2 \cdot 5\text{N}_2\text{H}_3\text{Ph}$ , obtained by adding excess of phenylhydrazine to a cold solution of cuprous chloride in 10 per cent. aqueous sodium chloride, crystallises in white needles; it begins to decompose at  $65^\circ$ , then becomes brown, and is rapidly decomposed at  $110^\circ$ .

*Phenylhydrazine cuprobromide*,  $2\text{Cu}_2\text{Br}_2 \cdot 7\text{N}_2\text{H}_3\text{Ph}$ , prepared by adding phenylhydrazine to cuprous bromide dissolved in aqueous potassium bromide, crystallises in slender, white needles which begin to decompose at  $70^\circ$  and undergo rapid decomposition at  $140^\circ$ .

*Phenylhydrazine cupro-iodide*,  $\text{Cu}_2\text{I}_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ , obtained by adding phenylhydrazine (4 mols.) to cuprous bromide (1 mol.) dissolved in 20 per cent. sodium thiosulphate solution, crystallises in rhomboidal prisms, and is somewhat more stable than the preceding salts. When heated, decomposition commences at  $100^\circ$ , and becomes very rapid at  $170^\circ$ .

When phenylhydrazine is added to solutions of cupric haloids, reduction occurs, and the corresponding cuprous compounds are

obtained. Cupric sulphate and nitrate, under the same conditions, yield pale rose-coloured, crystalline precipitates, too unstable to permit of isolation, which are probably compounds of phenylhydrazine with cuprous sulphate and nitrate respectively. Similar reactions are found to occur when precipitated copper is added to a mixture of cupric salts with pyridine. N. L.

**Action of Phenylhydrazine on Alkyl Bromides, Chlorides, and Iodides.** By JULES ALLAIN LE CANU (*Compt. rend.*, 129, 105—106. Compare Genvresse and Bourcet, this vol., i, p. 501).—To a well-cooled ethereal solution of phenylhydrazine (1 mol.) was added gradually and with constant stirring half a mol. of ethylic bromide free from hydrogen bromide; at the end of 24 hours, there was a deposit in slender needles of a compound, which, on analysis, proved to be a combination of two mols. of phenylhydrazine with one of hydrogen bromide; it melts and decomposes at 195°, and on prolonged heating at 100° loses one mol. of phenylhydrazine; it is slightly soluble in ether, soluble in alcohol, and very soluble in water; its aqueous solution is acid, and with silver nitrate gives a white precipitate which blackens rapidly. If alcohol is employed as solvent in place of ether, phenylhydrazine hydrobromide is the product.

The action of ethylic chloride on phenylhydrazine is similar to that of ethylic bromide, the analogous compounds being formed both in ethereal and alcoholic solutions; the hydrochloride containing 2 mols. of phenylhydrazine melts at about 225° and is less stable than the corresponding hydrobromide.

The compounds  $(\text{PhN}_2\text{H}_3)_2, \text{C}_8\text{H}_7\text{I}$  and  $(\text{PhN}_2\text{H}_3)_2, \text{C}_4\text{H}_9\text{I}$  are formed by the action of propylic iodide and normal butylic iodide respectively on phenylhydrazine; the former crystallises from alcohol in brilliant needles, is soluble in water, but only slightly so in ether, and melts at 122°; the latter has similar properties, and melts at 126°.

H. R. LE S.

**Action of Phenylhydrazine on Chloracetocarbamides and Chloracetylurethane.** By G. FRERICHs and HEINRICH BECKURTS (*Arch. Pharm.*, 1899, 237, 346—358).—The chloracetocarbamide,  $\text{NHR}^1\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$  [ $\text{R}=\text{H}, \text{Me}, \text{Ph}, \text{C}_6\text{H}_4\cdot\text{OEt}$ ] (1 mol.), was boiled for several hours with phenylhydrazine (2 mols.) in alcoholic solution; the alcoholic mother liquor contained yellow, resinous substances which have not yet been examined, whilst the solid which separated was in part soluble, in part insoluble, in very dilute hydrochloric acid. In the case of chloracetylurethane,  $\text{COOEt}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , no product soluble in hydrochloric acid was obtained.

The substances soluble in dilute hydrochloric acid were unsymmetrical phenylhydrazidacetocarbamides,  $\frac{1}{2}\text{NHR}^1\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{NH}_2$ . Phenylhydrazidaceto-carbamide, -methylcarbamide, -phenylcarbamide, and -4-ethoxyphenylcarbamide melt at 188°, 185°, 180°, and 169°, and their benzylidene derivatives at 219°, 238°, 177°, and 179° respectively. The first of these yields unsymmetrical phenylhydrazidacetic acid (Harries, *Abstr.*, 1895, i, 460), with evolution of ammonia, when it is boiled with aqueous caustic soda.

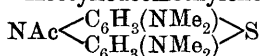
The substances insoluble in dilute hydrochloric acid, in the case of the phenylic and 4-ethoxyphenylic compounds, were oxidation products,  $\text{NHR} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{NHPh}$ , of the symmetrical phenylhydrazido-derivatives, which doubtless were first formed; *phenylhydrazine-glyoxyl-phenylcarbamide* and *-4-ethoxyphenylcarbamide* melt at  $197^\circ$  and  $151^\circ$  respectively. In the case of the methylic compound, the product was unfortunately lost. From chloracetocarbamide and -urethane, an identical product was obtained: probably a symmetrical phenylhydrazine, was formed as before, and then the central CO-group condensed with a second mol. of phenylhydrazine, when from the resulting compound, by elimination of ammonia in the one case and alcohol in the other, a compound,  $\text{NPh}-\text{N} \begin{array}{c} \diagup \\ \text{CO} \cdot \text{NH} \end{array} \text{C} \cdot \text{CH} \cdot \text{N} \cdot \text{NHPh}$ , was formed. This is yellowish, melts at  $275^\circ$ , and has a feebly acid character; a mono-silver derivative was prepared.

In the case of carbamide itself and of methylcarbamide the unsymmetrical derivatives form the main product; in the case of phenylcarbamide and 4-ethoxyphenylcarbamide about equal amounts of both derivatives are formed. This is in harmony with the fact, already recognised, that chloracetyl derivatives of radicles having an acid nature yield symmetrical derivatives of phenylhydrazine, whilst those of radicles having a basic nature yield unsymmetrical derivatives.

It has been shown in a previous paper (p. 806) that aromatic glycocinyl derivatives of carbamide readily yield  $\beta$ -hydantoins by elimination of ammonia. In a similar fashion, when unsymmetrical phenylhydrazidaceto-carbamide or -methylcarbamide is heated at about  $200^\circ$ , ammonia or methylamine is evolved and 1-phenyldiketotetrahydro- $\alpha$ -triazine,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{NPh} \\ \diagdown \quad \diagup \\ \text{NH} - \text{CO} \end{array} \text{CH}_2$ , is formed; this melts at  $229^\circ$  and has an acid character.

C. F. B.

**Acetylleucomethylene-Blue.** By GEORG COHN (*Arch. Pharm.*, 1899, 237, 385—390).—Acetylleucomethylene-blue,



(Berntsen, *Abstr.*, 1883, 917), was prepared by mixing methylene-blue hydrochloride (1 part) with glacial acetic acid (1 part) and acetic anhydride (3 parts), adding zinc powder gradually, and heating gently until all coloration had disappeared, then adding fused sodium acetate, boiling for 1—2 hours in a reflux apparatus, and finally pouring the product into water. It is colourless; it melts at  $179$ — $181^\circ$ , its *mercurichloride* melts at  $127^\circ$ , and its yellow *picrate* melts and decomposes at  $184$ — $185^\circ$ ; it is basic in character; various reagents convert it with moderate ease into a blue colouring matter, presumably methylene-blue; it is but little poisonous, and becomes oxidised to the blue colouring matter in the system.

*Acetylleucoethylene-blue*,  $\text{NAc} \begin{array}{c} \diagup \text{C}_6\text{H}_3(\text{NEt}_2) \\ \diagdown \text{C}_6\text{H}_3(\text{NEt}_2) \end{array} \text{S}$ , was prepared in the same way as the analogous methylene compound, and has similar properties; it melts at  $179$ — $180^\circ$ .

C. F. B.

**Symmetrical Dinitroditolylcarbamides.** By HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 659—665).—These compounds have been prepared by methods analogous to those employed in the preparation of the dinitrodiphenylcarbamides (this vol., i, 692), namely, by heating the various isomeric nitrotoluidines (2 mols.) with carbonyl chloride or with phenylic carbonate.

*Dinitroditolylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2)_2$  [ $\text{NH}:\text{Me}:\text{NO}_2=2:1:5$ ], from 5-nitroorthotoluidine, crystallises from boiling anhydrous acetic acid in small, white needles melting and subliming at  $305\text{--}310^\circ$ , and is insoluble in water, ether, benzene, or chloroform, slightly soluble in alcohol, more so in acetic acid. It is reduced by tin and hydrochloric acid to *diamidoditolylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2)_2$ , which crystallises from boiling 95 per cent. alcohol in small, white needles melting at  $264\text{--}265^\circ$ .

*Dinitroditolylcarbamide*, [ $\text{NH}:\text{Me}:\text{NO}_2=4:1:3$ ], from 3-nitroparatoluidine, crystallises from boiling acetic acid in yellow needles melting and subliming at  $244\text{--}245^\circ$ , and is soluble in alcohol or benzene, but insoluble in water. It is not reduced by stannous chloride, but when heated with zinc dust and acetic acid is converted into *diamidoditolylcarbamide*, which crystallises in slender, white needles and is insoluble in water or benzene, but slightly soluble in boiling alcohol; when heated, it sublimes without melting.

*Dinitroditolylcarbamide*, [ $\text{NH}:\text{Me}:\text{NO}_2=2:1:4$ ], from 4-nitroorthotoluidine, crystallises from boiling acetic acid in small, white needles melting and subliming at  $300\text{--}305^\circ$ , and is insoluble in water, benzene, chloroform, or ether, slightly soluble in alcohol, more so in boiling acetic acid. On reduction with tin and hydrochloric acid, it yields *diamidoditolylcarbamide*, which crystallises in white, microscopic needles, decomposes when heated, and is insoluble in water, benzene, or ether, but dissolves very slightly in boiling alcohol.

*Dinitroditolylcarbamide*, [ $\text{NH}:\text{Me}:\text{NO}_2=4:1:2$ ], from 2-nitroparatoluidine, is fairly soluble in boiling alcohol, acetic acid, or ethylic acetate, and crystallises either in white needles or in yellow prisms, in this respect resembling dimetanitrodiphenylcarbamide (*loc. cit.*). The two modifications melt at the same temperature,  $251\text{--}252^\circ$ , and when treated with tin and hydrochloric acid yield products having the characteristics of tolylenediamines mixed with a small quantity of *monamidoditolylcarbamide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$ ; when zinc dust and acetic acid are used, tolylenediamines alone are obtained.

3-Nitroparatoluidine, in which the  $\text{NO}_2$  and  $\text{NH}_2$  groups occupy the ortho-position with regard to each other, resembles orthonitraniline in entering into reaction with carbonyl chloride, but not with phenylic carbonate.

N. L.

**Action of Sulphuryl Chloride on Ethylic Metahydroxybenzoate.** By GIROLAMO MAZZARA (*Gazzetta*, 1899, 29, i, 371—383).—Whilst with ethylic salicylate, sulphuryl chloride gives rise to only one chloro-derivative (this vol., i, 700), in the case of ethylic metahydroxybenzoate two ethylic chlorohydroxybenzoates are obtained.

The acid corresponding with the ethylic salt comprising the liquid portion of the product is identical with the compound obtained by Peratoner and Condorelli (Abstr., 1898, i, 642), and has the constitution  $[\text{COOH} : \text{OH} : \text{Cl} = 1 : 3 : 6]$ ; it melts at  $178^\circ$ , the temperature given by Peratoner being  $169\text{--}170^\circ$ . *Methylic 6-chloro-3-hydroxybenzoate* separates from dilute alcohol in large, flat, glistening crystals melting at  $100^\circ$ . *Methylic 6-chloro-3-methoxybenzoate*,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COOMe}$ , is obtained as an oil, which on hydrolysis gives the methoxy-acid melting at  $168\text{--}169^\circ$ ; Peratoner and Condorelli (*loc. cit.*) give the melting point  $160\text{--}161^\circ$ .

The solid portion of the chlorinated product consists of a hydrated *ethylic chlorohydroxybenzoate*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COOEt} + \text{H}_2\text{O}$   $[\text{COOEt} : \text{OH} : \text{Cl} = 1 : 3 : ?]$ , crystallising from dilute alcohol in small, white needles, which, when heated, lose water and melt at  $58^\circ$  to a turbid liquid becoming transparent at a higher temperature; it is readily soluble in cold ether or alcohol, and when treated with benzene at the ordinary temperature or heated with light petroleum loses water, the anhydrous compound remaining in solution. The acid,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COOH}$ , melts at  $156\text{--}157^\circ$  and separates from benzene in prismatic plates, and from water in crystalline flocks; in aqueous solution, it gives a reddish-violet coloration with ferric salts. Its silver salt is a white, crystalline precipitate becoming violet on exposure to light. The *methylic* salt,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COOMe} + \text{H}_2\text{O}$ , crystallises from very dilute alcohol in long, white prisms melting at  $70\text{--}71^\circ$  with loss of water; the anhydrous *methylic* salt melts at  $62\text{--}65^\circ$ . *Methylic chloromethoxybenzoate*,  $[\text{COOMe} : \text{OMe} : \text{Cl} = 1 : 3 : ?]$ , separates from dilute alcohol in glistening needles melting at  $41\text{--}42^\circ$ . T. H. P.

**Action of Sulphuryl Chloride on Alkyllic Parahydroxybenzoates.** By GIROLAMO MAZZARA [and A. ROLAND] (*Gazzetta*, 1899, 29, i, 383—389).—*Methylic 3-chloro-4-hydroxybenzoate*,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COOH}$ , obtained by the interaction of sulphuryl chloride and ethylic parahydroxybenzoate in molecular proportions, separates from dilute alcohol in glistening, white, acicular crystals melting at  $107^\circ$ . The *methoxy*-derivative,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{COOMe}$ , is deposited from dilute alcohol in sparkling, white crystals melting at  $93\text{--}94^\circ$ .

Ethylic 3-chloro-4-hydroxybenzoate, prepared by the interaction of sulphuryl chloride and ethylic parahydroxybenzoate, in molecular proportion, crystallises from alcohol in sparkling, flocky needles melting at  $77\text{--}78^\circ$ .

*Ethylic 3:5-dichloro-4-hydroxybenzoate*, obtained by the action of two mols. of sulphuryl chloride on one of ethylic parahydroxybenzoate, separates from dilute alcohol in small, white, acicular crystals melting at  $116^\circ$ , and is soluble in benzene or light petroleum. The acid melts at  $257\text{--}258.5^\circ$ ; Lössner gives  $255\text{--}256^\circ$  and Zincke  $259\text{--}260^\circ$ .

By the action of two mols. of sulphuryl chloride on one of *methylic* parahydroxybenzoate, *methylic 3:5-dichloro-4-hydroxybenzoate* melting at  $121^\circ$  is obtained.

A table is given of all the products obtained by the action of sulphuryl chloride on alkyllic hydroxybenzoates. T. H. P.

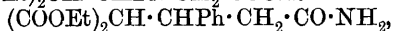
**Influence of Carbonyl on Adjacent Groups.** By DANIEL VORLÄNDER (*Chem. Centr.*, 1899, i, 729; from *Abhand. Naturforsch. Ges. Halle*, 21, 233—250).—The proximity of the carbonyl group renders the hydrogen atoms attached to  $\alpha$ -carbon atoms more easily replaceable, and two carbonyl or negative groups ( $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot$  or  $\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CN}$ ) may even cause the hydrogen atoms to be capable of ionisation (compare von Schilling and Vorländer, *Annalen*, 1899, 308, 184). The proximity of a carbonyl group to a double linking ( $\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot$ ), confers the additive properties of ethylic sodiomalonate, &c., on  $\alpha\beta$ -unsaturated alkyl salts and ketones. Phenylethylene and the following derivatives,  $\text{C}_8\text{H}_7\cdot\text{Ph}$ ,  $\text{C}_8\text{H}_7\cdot\text{NO}_2$ ,  $\text{C}_8\text{H}_7\cdot\text{C}_5\text{NH}_6$ ,  $\text{C}_8\text{H}_7\cdot\text{CH}:\text{N}\cdot\text{NHPH}$ ,  $\text{C}_8\text{H}_7\cdot\text{CMe}:\text{N}\cdot\text{NHPH}$ , are incapable of forming additive compounds with compounds of the type of  $\text{NaHC}(\text{COOR})_2$ . The following derivatives of cinnamic acid combine with alkyl salts of sodiomalonic acid,  $\text{C}_8\text{H}_7\cdot\text{COOEt}$  (6),  $\text{C}_8\text{H}_7\cdot\text{COMe}$ ,  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NH}_2$ ,  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NHMe}$  (43),  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NHEt}$  (44),  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NHPH}$ ,  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NMe}_2$  (29),  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NEt}_2$  (46),  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{C}_5\text{NH}_{10}$  (28),  $\text{C}_8\text{H}_7\cdot\text{CO}\cdot\text{NPh}_2$  (32), the numbers in brackets referring to the percentages of each compound which remain uncombined after the reaction has gone on for 6 hours. There is apparently no fundamental difference between the alkyl salts and the amides. The more or less positive character of the amine also has little influence, and tertiary and secondary amines behave in a like manner.

E. W. W.

**Behaviour of Unsaturated Compounds towards Ethylic Malonate.** By PAUL HERRMANN and DANIEL VORLÄNDER (*Chem. Centr.*, 1899, i, 730—731; from *Abhand. Naturforsch. Ges. Halle*, 21, 251—270).—The unsaturated compounds were treated with ethylic sodiomalonate by dissolving them in alcohol together with sodium, adding ethylic malonate, and boiling the mixture for 6 hours.

I. Unsaturated compounds not containing carbonyl. By the action of ethylic sodiomalonate on styrene, metastyrene is formed. Phenylnitroethylene is partly polymerised, forming a slightly soluble, white, amorphous compound,  $(\text{C}_8\text{H}_7\cdot\text{NO}_2)_x$ , which melts at  $280^\circ$ . Stilbene, benzylidenequininaldine, cinnamaldehydephenylhydrazone, and benzylideneacetophenonehydrazone are not attacked.

II. Unsaturated compounds containing carbonyl. Alkyl cinnamates and cinnamamides all combine with ethylic sodiomalonate, forming the compounds  $(\text{COOEt})_2\text{CH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COOEt}$  and

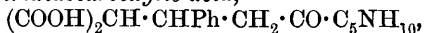


which, when hydrolysed with cold sodium hydroxide solution, yield phenylglutarcarboxylic acid and phenylglutaramidocarboxylic acid respectively. The former is easily soluble in water. Phenylglutaramidocarboxylic acid and most of its derivatives dissolve easily in dilute hydrochloric acid and cannot be separated from the unchanged cinnamic acid, but by heating them with concentrated hydrochloric acid, carbonic anhydride is eliminated and  $\beta$ -phenylglutaric acid,  $\text{C}_{11}\text{H}_{12}\text{O}_4$ , is formed. An almost quantitative yield of this acid is also obtained by treating ethylic cinnamate with sodium ( $1-1\frac{1}{2}$  ats.); it crystallises from water in white, prismatic plates, melts at  $138^\circ$ , is slightly soluble in benzene, and is only attacked by alkaline solutions

of potassium permanganate with difficulty. The *ammonium* salt crystallises in hexagonal leaflets and is stable in air. *Dimethylic β-phenylglutarate* crystallises in small, white needles or leaflets and melts at 86—87°. *β-Phenylglutaric anhydride*,  $C_{11}H_{10}O_3$ , prepared by the action of boiling acetic anhydride on the acid, crystallises from benzene, melts at 105°, boils at 217—219° under 15 mm. pressure, is slightly soluble in chloroform, and easily so in carbon bisulphide or boiling benzene. *β-Phenylglutarimide*,  $CHPh \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} NH$ , crys-

tallises from water in small leaflets, melts at 173—174°, is insoluble in solutions of sodium carbonate, ammonia, or dilute hydrochloric acid, but dissolves in cold sodium hydroxide solution. *β-Phenylglutaranilic acid*,  $COOH \cdot CH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot NHPh$ , obtained by the action of aniline on the anhydride, crystallises from dilute alcohol in small needles, melts at 171°, and is easily soluble in sodium carbonate solution. The amides of cinnamic acid, with the exception of the anilide and the diphenylamide, are all soluble in hydrochloric acid. By the action of ethylic sodiomalonate on cinnamamide, a sodium salt is formed which, by the action of carbonic anhydride, yields the compound,  $CHPh \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}(\text{COOEt}) \cdot \text{CO} \end{smallmatrix} NH$ ; it crystallises

from water in small needles, melts at 119°, is soluble in alkalis and in excess of hydrochloric acid, and when boiled with hydrochloric acid forms phenylglutaric acid. *Cinnamomethylamide*,  $C_{10}H_{11}NO$ , crystallises from water, melts at 110—111°, and is easily soluble in hot benzene or alcohol; it forms an additive compound with ethylic sodiomalonate which decomposes into phenylglutaric acid. *Cinnamodimethylamide*,  $C_{11}H_{13}NO$ , crystallises from water in small needles or leaflets and melts at 96°. *Cinnamoethylamide*,  $C_{11}H_{13}NO$ , crystallises from water and melts at 92—93°. *Cinnamodiethylamide*,  $C_{13}H_{17}NO$ , crystallises from very dilute alcohol in needles or prisms, melts at 66°, is very easily soluble in benzene or alcohol, and combines with bromine to form the diethylamide of phenyldibromopropionic acid,  $C_{13}H_{17}NOBr_2$ , which crystallises from alcohol in white prisms and melts at 127°. *Phenylglutarodiethylamidocarboxylic acid* melts at 147°, with liberation of carbonic anhydride. *Cinnamopiperidide*,  $C_{14}H_{17}NO$ , when treated with bromine, forms the piperidide of phenyldibromopropionic acid,  $C_{14}H_{17}NOBr_2$ , which crystallises from alcohol in long needles and melts and decomposes at 189°. When cinnamopiperidide is treated with ethylic sodiomalonate and the product hydrolysed, *phenylglutaropiperidocarboxylic acid*,

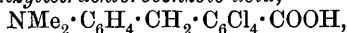


is obtained; it crystallises from water in white prisms, melts and decomposes at 146°, is easily soluble in alcohol, slightly so in benzene, is precipitated from alkaline solutions by small quantities of dilute hydrochloric acid, dissolves on the addition of more acid, but on shaking separates from the solution in a crystalline form. The *piperidide of phenylglutaric acid*,  $COOH \cdot CH_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot C_5NH_{10}$ , prepared from the piperididocarboxylic acid by eliminating carbonic anhydride, crystallises from alcohol in white leaflets and melts at 120°. *Cinnamodiphenylamide* melts at 154° and combines with ethylic

sodiummalonate almost as readily as the piperidide. Cinnamanilide, when treated with ethylic sodiummalonate, forms the *anilide* of *ethylic phenylglutarate*,  $\text{CHPh} \begin{array}{c} \text{CH}(\text{COOEt}) \cdot \text{CO} \\ \text{CH}_2 \text{---} \text{CO} \end{array} \text{NPh}$ , and the *sodium salt* of an *acid anilide*. The former crystallises from alcohol in small, white needles, melts at  $166^\circ$ , is insoluble in ammonia or sodium carbonate solution, and by the action of cold potassium hydroxide solution forms the anilidocarboxylic acid, which, by elimination of carbonic anhydride, yields the phenylanilidoglutaric acid,  $\text{C}_{17}\text{H}_{17}\text{NO}_3$ , melting at  $169^\circ$ . The acid anilide salt is not easily obtained pure; it forms small crystals, melts and decomposes at  $85\text{--}90^\circ$ , by the action of boiling hydrochloric acid yields phenylglutaric acid, and when decomposed with cold potassium hydroxide solution gives the same products as the preceding compound. A third compound, the *potassium salt* of an *acid*, is obtained by hydrolysing the original alcoholic solution with cold potassium hydroxide solution; it crystallises from dilute alcohol in prisms, melts at  $150\text{--}152^\circ$ , and decomposes into cinnamic acid. Cinnamonitrile combines with ethylic sodiummalonate to form an oily substance which, by the action of hydrochloric acid, yields phenylglutaric acid. E. W. W.

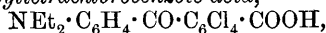
**Dialkylbenzoyl- and Dialkylbenzyl-benzoic Acids.** By ALBIN HALLER and HERM. UMBGROVE (*Compt. rend.*, 1899, 129, 90—92. Compare Abstr., 1898, i, 670).—*Dimethylamidobenzoyltetrachlorobenzoic acid*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{Cl}_4 \cdot \text{COOH}$ , prepared by the action of dimethylaniline on tetrachlorophthalic anhydride in the presence of aluminium chloride, forms yellow scales melting at  $211^\circ$ , and is nearly insoluble in water, but somewhat readily soluble in alcohol or ether. It is not nitrated by a mixture of sulphuric and nitric acids. *Dimethylamidobenzoyltetrachlorobenzoic acetic anhydride*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{Cl}_4 \cdot \text{COOAc}$ , obtained by warming a mixture of the tetrachlorobenzoic acid and dimethylaniline with acetic anhydride, crystallises in colourless scales, melts at  $196^\circ$ , and is soluble in benzene, but only slightly so in alcohol. The *methyl salt*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{Cl}_4 \cdot \text{COOMe}$ , could not be prepared by the action of hydrogen chloride on a methyl alcohol solution of the acid, but was obtained by treating the mixed anhydride with the calculated amount of sodium methoxide. It forms yellow crystals and melts at  $167^\circ$ . The *ethylic salt*, prepared in the same way, forms yellow needles melting at  $143^\circ$ .

*Dimethylamidobenzoyltetrachlorobenzoic acid*,



was obtained by reduction of the benzoyl acid with zinc dust and hydrochloric acid; it forms slender, white needles, melts at  $215^\circ$ , and is very soluble in alcohol, but less so in boiling water or ether.

*Diethylamidobenzoyltetrachlorobenzoic acid*,



obtained in the same way as the methyl derivative, forms yellow crystals, melts at  $222^\circ$ , is very soluble in ethylic alcohol, but much less so in methyl alcohol or in benzene, and nearly insoluble in water; it is not nitrated by a mixture of nitric and sulphuric acids. *Diethylamidobenzoyltetrachlorobenzoic acetic anhydride* crystallises in



colourless scales, melts at  $175^{\circ}$ , and is soluble in benzene. The *methyl*ic salt forms yellow crystals melting at  $160^{\circ}$ , and the *ethyl*ic salt yellow crystals melting at  $135^{\circ}$ .  
H. R. LE S.

**Orthotolylamidoacetic Acid.** By W. HENTSCHEL (*J. pr. Chem.*, 1899, [ii], 60, 80—84).—When purified by crystallisation from dilute sulphuric acid, orthotolylamidoacetic acid melts at  $160^{\circ}$ , and not at  $149$ — $150^{\circ}$ ; when boiled with water or mineral acids, or when heated to  $220^{\circ}$ , it loses carbonic anhydride and gives methylorthotoluidine. The glycocine forms a *hydrochloride* and a sparingly soluble *nitrate*, but not a sulphate, the base crystallising from dilute sulphuric acid; the metallic salts are much more stable. The *calcium* salt gives pure orthotoluidine when distilled. The *ethyl*ic salt is an oil boiling at  $280^{\circ}$ ; when left for some time, it partially solidifies, forming large, transparent crystals which melt at  $26^{\circ}$ . *Dichlororthotolylamidoacetic acid* crystallises from hot dilute alcohol in needles and melts at  $160$ — $162^{\circ}$ ; when heated above the melting point, it loses carbonic anhydride and is converted into the dichloromethylorthotoluidine boiling at  $258$ — $259^{\circ}$ .  
T. M. L.

**Dimethylanilidophthaloylic Acid.** By HEINRICH LIMPRICHT [and H. SEYLER] (*Annalen*, 1899, 307, 305—313. Compare Abstr., 1898, i, 435; also Haller and Guyot, Abstr., 1898, i, 593 and 670).—Haller and Guyot having claimed priority to the subject investigated by the author (*loc. cit.*), a description of the work is now placed on record.

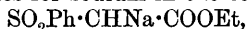
*Dimethylamidohydroxybenzophenone*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , produced when dimethylanilidophthaloylic acid is heated at  $260^{\circ}$  under 20 mm. pressure, crystallises from alcohol in lustrous, white scales, and melts at  $187^{\circ}$ . When dimethylanilidophthaloylic acid is distilled with baryta, paradimethylamidobenzophenone is formed, melting at  $91^{\circ}$ .

The *chloride* of dimethylanilidophthaloylic acid,  
 $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ ,  
obtained by treating the acid with phosphorus pentachloride suspended in carbon bisulphide, crystallises in white prisms softening at  $115^{\circ}$ ; methylic alcohol converts it into methylic dimethylanilidophthaloylate, which melts at  $118^{\circ}$  (Haller and Guyot give  $128^{\circ}$ ).

*Nitrodimethylanilidophthaloylic acid*,  
 $\text{NMe}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH} + \text{H}_2\text{O}$ ,  
prepared by slowly adding concentrated nitric acid mixed with concentrated sulphuric acid to a solution of dimethylanilidophthaloylic acid in concentrated sulphuric acid, separates from alcohol in yellow crystals and melts at  $114$ — $115^{\circ}$ ; the *silver* salt crystallises in yellow needles and blackens in light, and the methylic salt melts at  $163^{\circ}$ .

*Dimethylanilidophenylmethane*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Ph}$ , produced when dimethylanilidohydrophthaloylic acid is distilled with baryta, is probably identical with the base obtained by Michler and Gradmann (Abstr., 1888, 299) on heating dimethylphenylbenzylammonium chloride; it forms colourless leaflets melting at  $31^{\circ}$ , and the *hydrochloride* begins to decompose at  $115^{\circ}$ . The *nitroso*-derivative separates from alcohol in orange-red crystals and melts at  $89^{\circ}$ .  
M. O. F.

**Substitution of Alkyl Radicles for Sodium in Ethylic Phenylsulphonesodioacetate.** By ARTHUR MICHAEL (*J. pr. Chem.*, 1899, [ii], 60, 96).—The earlier work of Comey and Michael (*Abstr.*, 1884, 319) and of Palmer and Michael (*Abstr.*, 1885, 986) on the substitution of alkyl radicles for sodium in the compound



has been repeated and confirmed. The statements of Otto and Rössing (*Abstr.*, 1889, 994) to the effect that this substitution does not take place are therefore without foundation. T. M. L.

**Mercuriphenyl Sulphide and Thiosulphate.** By LEONE PESCI (*Gazzetta*, 1899, 29, i, 394—399).—*Mercuriphenyl sulphide*,  $(\text{PhHg})_2\text{S}$ , obtained by the action of hydrogen sulphide or an alkali sulphide on a solution of mercuriphenyl acetate in ammoniacal ammonium acetate, is a white, amorphous powder insoluble in water or alcohol, but soluble in chloroform, giving a solution which rapidly changes, a yellow powder being deposited. Hot fuming hydrochloric acid dissolves it, but the cold dilute acid blackens it, hydrogen sulphide being evolved in both cases. Heated at  $108^\circ$ , it decomposes and becomes black, and when boiled in a reflux apparatus with alcohol, it is split up into mercuric sulphide and mercury diphenyl. It is soluble in cold carbon bisulphide, and the solution deposits first colourless, silky needles and afterwards a yellowish substance which only partially redissolves in carbon bisulphide, and is shown to be *mercuriphenyl thiocarbonate*,  $(\text{PhHg})_2\text{CS}_3$ . This compound is insoluble in water or alcohol, slightly soluble in ether or benzene, more so in chloroform, and is completely dissolved by hot fuming hydrochloric acid. At  $108^\circ$ , it blackens, mercuric sulphide being formed and carbon bisulphide evolved, and when heated with benzene, it decomposes rapidly with the production of mercuric sulphide and mercury diphenyl.

*Mercuriphenyl thiosulphate*,  $(\text{PhHg})_2\text{S}_2\text{O}_3$ , prepared by adding a solution of 1 mol. of sodium thiosulphate to a solution of 2 mols. of mercuriphenyl acetate in ammoniacal ammonium acetate, is a white, amorphous precipitate insoluble in the ordinary solvents, but soluble in concentrated hydrochloric acid with the evolution of sulphurous anhydride and separation of sulphur. It is apparently unchanged when heated at  $200^\circ$ , and dissolves readily in aqueous sodium thiosulphate, giving a solution which, on standing, deposits mercury diphenyl. T. H. P.

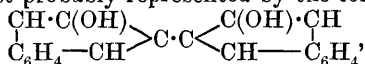
**Chemistry of Lignite Tar.** By EUGEN OEHLER (*Zeit. angew. Chem.*, 1899, 561—563).—The alkaline solution obtained in the extraction of creosote from the crude oil by means of aqueous caustic soda of  $40^\circ$  Beaumé (sp. gr. 1.375) contains, in solution, some oil ("neutral creosote") which is liberated upon dilution with water. This oil has been examined and found to have essentially the same composition as the original oil; in addition to unsaturated substances removable by strong sulphuric acid, nonane, decane, toluene, metaxylene, and naphthalene were detected in it. Much the same substances were also detected in neutral creosote from paraffin oil; in this, undecane was found. Attention was also paid to the bases extracted

from the crude oil with sulphuric acid, and aniline was detected amongst these.

A new *hydrocarbon*,  $C_{16}H_{18}$ , which melts at  $117^\circ$ , boils at  $300\text{--}303^\circ$ , and forms a red *picrate*,  $C_{16}H_{18}, C_6H_3N_3O_7$ , melting at  $154^\circ$ , has been isolated from a press-oil, poor in paraffin. A middle fraction of this was distilled several times until about 80 per cent. passed over at  $290\text{--}320^\circ$ . In this fraction, about 8 per cent. of its weight of picric acid was dissolved with the aid of heat, and the picrate which separated on cooling was washed with light petroleum and decomposed with ammonia; the fraction contained about 0.5 per cent. of the hydrocarbon in question. C. F. B.

**Derivatives of Unsymmetrical Tetramethyldiamidodiphenylethane.** By AUGUSTE TRILLAT (*Compt. rend.*, 1899, 128, 1404—1406. Compare this vol., i, 615).—The following derivatives of unsymmetrical tetramethyldiamidodiphenylethane are described: The *hydrochloride*,  $C_{18}H_{24}N_2, 2HCl$ , forms a white, crystalline powder decomposing at  $225^\circ$ ; it is soluble in alcohol or water, but almost insoluble in acetone; the *dihydrogen sulphate*,  $C_{18}H_{24}N_2, 2H_2SO_4$ , is hygroscopic and melts at  $188\text{--}189^\circ$ ; the *acetate* crystallises in long needles which redden on exposure to air. The *ethobromide*,  $C_{18}H_{24}N_2, 2EtBr$ , melts and decomposes at  $224\text{--}225^\circ$ , and is soluble in alcohol or water, but insoluble in acetone; the *ethiodide*,  $C_{18}H_{24}N_2, 2EtI$ , decomposes at  $228\text{--}230^\circ$ . Unstable compounds,  $C_{18}H_{21}Br_2N_2$  and  $C_{18}H_{21}I_2N_2$ , are obtained by the action of bromine and iodine respectively on the base dissolved in acetic acid. The *dinitro-derivative*,  $C_{18}H_{22}N_2(NO_2)_2$ , prepared by adding cold fuming nitric acid to an acetic acid solution of the base, crystallises in pale yellow prisms melting at  $195\text{--}196^\circ$ ; polynitro-derivatives are obtained when the nitration is performed in the presence of sulphuric acid. Paranitrodimethylaniline is produced when sodium nitrite is added to a solution of the base in cold acetic acid. G. T. M.

**Constitution of  $\beta\beta$ -Dinaphthol.** By R. FOSSE (*Bull. Soc. Chim.*, 1899, [iii], 21, 650—653).—The constitution of  $\beta\beta$ -dinaphthol (this vol., i, 529) is most probably represented by the formula



which explains the formation of *aa*-dinaphthyl when  $\beta\beta$ -dinaphthol is heated with zinc dust, and its conversion into ortho- $\beta$ -hydroxynaphthoylbenzoic acid by oxidation with potassium permanganate. It is in accordance with the ready transformation of  $\beta\beta$ -dinaphthol into dinaphthylene oxide, and into an imine instead of a diamine, and also with the fact that no aldehydic compound could be obtained by Reimer and Tiemann's reaction. N. L.

**Some New Derivatives of  $\beta\beta$ -Dinaphthol.** By R. FOSSE (*Bull. Soc. Chim.*, 1899, [iii], 21, 655—659).— $\beta\beta$ -Dinaphthol reacts with propionic chloride to form a *dipropionate*,  $C_{20}H_{12}(O\cdot CO\cdot CH_2Me)_2$ , which crystallises from alcohol in transparent needles melting at  $105^\circ$ . The *dibutyrate*,  $C_{20}H_{12}(O\cdot CO\cdot CH_2\cdot CH_2Me)_2$ , prepared in a similar manner from butyric chloride, crystallises from alcohol in short, slender needles melting at  $207^\circ$ . The *phthalate*,  $C_{20}H_{12}\begin{array}{c} \text{O}\cdot\text{CO} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CO} \end{array} \text{C}_6\text{H}_4$ ,

is a white, crystalline substance which melts and decomposes at  $215^{\circ}$ . Unsuccessful attempts were made to prepare a phthalein by the action of phthalic anhydride on  $\beta\beta$ -dinaphthol. *Dinaphthyl isopropyl ether*,  $C_{20}H_{12}(O\cdot CHMe_2)_2$ , is crystalline and melts at  $150^{\circ}$ . *Dibromo- $\beta\beta$ -dinaphthol*,  $C_{20}H_{12}Br_2O_2$ , obtained by adding the theoretical amount of bromine to a solution of  $\beta\beta$ -dinaphthol in acetic acid, melts at  $155^{\circ}$ , and is very soluble in alcohol and ether. Its *potassium* derivative crystallises in colourless, striated prisms, and the *sodium* derivative is a crystalline powder; these compounds rapidly turn brown on exposure to air, but are more stable than the corresponding alkali derivatives of  $\beta\beta$ -dinaphthol. *Dichlorodinaphthylene oxide*,  $C_{20}H_{10}Cl_2O$ , obtained by heating a solution of  $\beta\beta$ -dinaphthol in carbon bisulphide with sulphuryl chloride, crystallises in yellow needles melting at  $165^{\circ}$ . It gives a violet coloration with sulphuric acid, and is isomeric with the substance, melting at  $245^{\circ}$ , produced by the action of phosphorus pentachloride on dinaphthylene oxide. N. L.

**Action of Aldehydes and Aldehydic Chlorides on  $\beta\beta$ -Dinaphthol: Acetals.** By R. FOSSE (*Bull. Soc. Chim.*, 1899, [iii], 21, 653—655. Compare this vol., i, 529).— $\beta\beta$ -Dinaphthol does not enter into reaction with aldehydes in the presence of sulphuric acid, zinc chloride, or hydrogen chloride, but when heated with aldehydic chlorides,  $R\cdot CHCl_2$ , and alcoholic potash or sodium ethoxide, compounds analogous to acetal are obtained in nearly theoretical quantity. *Dinaphthyl benzylidenic ether*,  $C_{20}H_{12}\langle\begin{smallmatrix} O \\ \diagup \quad \diagdown \end{smallmatrix}\rangle CHPh$ , from  $\beta\beta$ -dinaphthol and benzylidenic chloride, is crystalline, and melts at  $128^{\circ}$ . *Dinaphthyl ethylidenic ether*,  $C_{20}H_{12}\langle\begin{smallmatrix} O \\ \diagup \quad \diagdown \end{smallmatrix}\rangle CHMe$ , from  $\beta\beta$ -dinaphthol and ethylidenic chloride, is a crystalline substance melting at  $112^{\circ}$ . These compounds are decomposed by dilute acids and concentrated alkalis, with the formation of  $\beta\beta$ -dinaphthol and benzoic and acetic aldehydes respectively. N. L.

**Diphenylanthrone Derivatives.** By L. TÉTRY (*Compt. rend.*, 1899, 128, 1406—1407. Compare Abstr., 1898, i, 483).—*Methoxydiphenylanthrone*,  $OMe\cdot C_6H_4\cdot CPh\langle\begin{smallmatrix} C_6H_4 \\ \diagup \quad \diagdown \\ C_6H_4 \end{smallmatrix}\rangle CO$ , obtained by condensing anisole with chlorophenylanthrone in carbon bisulphide solution in the presence of aluminium chloride, crystallises in colourless prisms melting at  $180$ — $181^{\circ}$ ; it is soluble in the ordinary organic solvents, and, like other compounds of this group, develops a yellow coloration with concentrated sulphuric acid. *Ethoxydiphenylanthrone* melts at  $159$ — $160^{\circ}$ , and in properties resembles its lower homologue; it separates from benzene in colourless prisms containing 1 mol. of this solvent.

*Dimethylamidodiphenylanthrone*,  $NMe_2\cdot C_6H_4\cdot CPh\langle\begin{smallmatrix} C_6H_4 \\ \diagup \quad \diagdown \\ C_6H_4 \end{smallmatrix}\rangle CO$ , is prepared by substituting dimethylaniline for anisole in the condensation. The base crystallises in transparent, yellow prisms melting at  $215^{\circ}$ ; its salts are dissociated by water. *Diethylamidodiphenylanthrone* crystallises from toluene in transparent, yellow, dichroic prisms which contain  $\frac{1}{2}$  mol. of toluene; it melts at  $194$ — $195^{\circ}$ . The colour of these bases is less intense than that of the corresponding dialkylamido-

anthraquinones, diphenylanthrone, which contains only one carbonyl chromophore, being a weaker chromogen than anthraquinone.

G. T. M.

**Dimethyldianthracene, a Polymeride of  $\beta$ -Methylantracene.** By WILLIAM R. ORNDORFF and H. A. MEGRAW (*Amer. Chem. J.*, 1899, 22, 152—157).—When  $\beta$ -methylantracene, suspended in benzene, is exposed to the action of sunlight, it is rapidly polymerised into *dimethyldianthracene*,  $(C_{15}H_{12})_2$ , just as anthracene, under similar conditions, gives rise to dianthracene (Orndorff and Cameron, *Abstr.*, 1896, i, 176); the product crystallises from toluene in small, probably orthorhombic, crystals and melts at 228—230°, decomposing partially into  $\beta$ -methylantracene. Its molecular weight was determined by the boiling point method, using toluene and pyridine as solvents. Unlike  $\beta$ -methylantracene, it is non-fluorescent, and does not form a compound with picric acid. It is very sparingly soluble in all the ordinary solvents, but when boiled for a long period with anisole or metaxylene, becomes partially soluble owing to conversion into  $\beta$ -methylantracene.

W. A. D.

**Optical Rotation of Pinene Hydrochloride.** By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1899, 21, 637—642).—Pinene hydrochloride melts at 131°, and not at 125° as stated by Pesci (*Abstr.*, 1889, 158) and others. Various values have been given by different authorities for the specific rotatory power of the hydrochloride (compare Berthelot *Ann. Chim. Phys.*, 1854, [iii], 40, 5; Flawitzky, *Ber.*, 1882, 15, 5; Marsh and Gardner, *Trans.*, 1891, 59, 725; Pesci, *loc. cit.*; Wallach and Conrady, *Abstr.*, 1889, 1072). The different values—from 0° to +30°—are due to the fact that the hydrocarbon employed by the different authorities contained varying amounts of *d*- and *l*-pinene. From experiments made by the author, it appears that the hydrochloride of *l*-pinene has a higher rotatory power than *l*-pinene, whereas the hydrochloride from *d*-pinene has a slightly lower rotatory power than *d*-pinene. J. J. S.

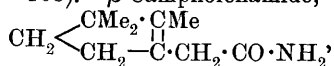
**Crystallographic Relations of Optically Active Substances and their Racemic Compounds [Pinonic Acids].** By ANDREAS FOCK (*Zeit. Kryst. Min.*, 1899, 31, 479—483).—Optically active substances may be divided into three groups: (1) those with no racemic compounds, the two antipodes crystallising separately from the mixed solution; for example, asparagine and *cis*- $\pi$ -camphanic acid; (2) those in which the antipodes unite in constant proportions to form a racemic compound, for example, tartaric acid and tartrates; (3) those in which the antipodes unite in varying proportions to form numerous racemic or pseudoracemic compounds, for example, limonene tetrabromide and brucine valerate. Between groups (1) and (2) there is a connecting link, thus the racemate,  $(C_4H_4O_6NaNH_4)_2 + 2H_2O$ , is formed from the two tartrates above 27°, whilst below this temperature the two antipodes crystallise separately. A connecting link between groups (2) and (3) is now described.

The optically active pinonic acid crystallises in tetragonal pyramids, and the two antipodes have the same form [ $\alpha:c=1:1\cdot12757$ ]. Circular polarisation could not be observed in the imperfect crystals, but their solutions show wide variations in the rotatory power; in the *lævo*-acid,  $[\alpha]_D$  reaches 20°, and in the *dextro*-acid,  $[\alpha]_D$  may reach 130°.

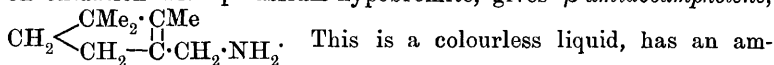
This variation is to be explained by the capability of the two modifications mixing together as isomorphous substances. The racemic compound of the two active pinonic acids forms tabular, monoclinic crystals [ $\alpha : b : c = 0.6445 : 1 : 0.5585$ ;  $\beta = 76^\circ 8'$ ]. Solutions of these crystals show rotations up to  $[\alpha]_D = 10^\circ$ . The two active compounds must therefore, to a certain extent, crystallise isomorphously with the racemic compound, giving a passage between groups (2) and (3). This would be expected to take place in the pseudo-racemic compounds, the crystalline forms of which differ only slightly from those of the corresponding active substances.

Amongst inorganic salts, group (2) is represented by double salts and (3) by isomorphous mixtures, and there are also analogous connecting links between the groups. L. J. S.

**Amidocampholenes.** By EDMOND E. BLAISE and G. BLANC (*Compt. rend.*, 1899, 129, 106—108).— $\beta$ -Campholenamide,

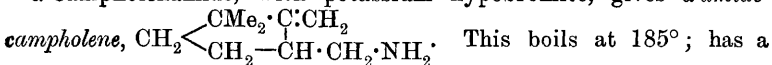


on oxidation with potassium hypobromite, gives  $\beta$ -amidocampholene,



This is a colourless liquid, has an amoniacal odour, and boils at  $185^\circ$  under atmospheric pressure; it has a sp. gr. 0.8778 at  $15^\circ$ , and a molecular refraction  $n_D$  44.83. The *hydrochloride* crystallises in long needles melting at  $194$ — $195^\circ$ , the *platinochloride* decomposes above  $200^\circ$ , the *picrate* melts at  $228$ — $229^\circ$ , and the *oxamide* at  $111$ — $112^\circ$ . By interaction with potassium cyanate, the hydrochloride forms a substituted *carbamide* melting at  $108$ — $109^\circ$ .

$\alpha$ -Campholenamide, with potassium hypobromite, gives  $\alpha$ -amido-



This boils at  $185^\circ$ ; has a sp. gr. 0.8795 at  $15^\circ$ , and a molecular refraction  $n_D$  44.88. The *hydrochloride* forms small prisms melting at  $253^\circ$ , the *picrate* melts at  $219^\circ$ , and the *oxamide* crystallises in needles fusing at  $131^\circ$ . With potassium cyanate, a substituted *carbamide* is formed melting at  $119$ — $120^\circ$ .

$\alpha$ - and  $\beta$ -Amidocampholenes, on reduction, should both give an amidodihydrocampholene identical with that prepared by one of the authors from isolaunonic nitrile (Blanc, *Bull. Soc. Chim.*, 1899, [iii], 21, 322). Attempts were therefore made to obtain this from each, but instead of the amidodihydrocampholene, a base was obtained the boiling point of which was much higher than that of the compound sought. H. R. LE S.

**Cascara Sagrada.** By LEPRINCE (*Compt. rend.*, 1899, 129, 60—61).—If cascara sagrada, the bark of *Rhamnus purshiana*, is extracted with 5 per cent. aqueous soda and the liquid acidified, a precipitate is obtained which consists chiefly of chrysarobin, chrysophanic acid, and emodin. Details of the separation and identification of these substances are given in the paper. N. L.

**Aloins.** By EUGÈNE LÉGER (*Compt. rend.*, 1899, 128, 1401—1403. Compare Abstr., 1898, i, 445; this vol., i, 157).—Finely ground Natal aloes were digested with cold acetone to remove resinous matters, and

then extracted with boiling methylic alcohol and filtered; the filtrate, on cooling, deposited yellow, lamellar crystals which were separated into two constituents by fractional crystallisation from the same solvent.

*Nataloin*,  $C_{16}H_{18}O_7$ , the more soluble compound, forms pale yellow scales less soluble in methylic alcohol than barbaloin, and insoluble in hot water or ether. Like barbaloin, it possesses a phenolic character, and dissolves in alkaline solutions, from which it is reprecipitated by carbonic anhydride. It dissolves in ammonia or pyridine, but combines with acids less readily than barbaloin. Acetic chloride forms with it a small quantity of a crystalline *acetyl* derivative separating in octahedra and in scales, but the principal product is a yellow, amorphous substance very soluble in ether. *Tribenzoyl-nataloin*,  $C_{16}H_{15}O_7Bz_3$ , obtained by the action of benzoic chloride on nataloin in pyridine solution, forms a yellow, tumid mass very soluble in ether or alcohol, but insoluble in water or dilute solutions of the alkalis; it is devoid of bitter taste. The *tetrabenzoyl* derivative,  $C_{16}H_{14}O_7Bz_4$ , obtained by heating the aloin with benzoic chloride in sealed tubes at  $100^\circ$ , separates from alcohol in yellow, amorphous granules.

*Homonataloin*,  $C_{15}H_{16}O_7$ , the less soluble constituent of the crude aloin, separates from methylic alcohol in nodular masses of yellow lamellæ; its *acetyl* derivative is amorphous. The *tri-* and *tetrabenzoyl* derivatives,  $C_{15}H_{13}O_7Bz_3$  and  $C_{15}H_{12}O_7Bz_4$  are obtained in brick-red granules.

These aloins develop a green coloration with sulphuric acid and manganese dioxide or potassium dichromate, and a violet with a soda solution containing ammonium persulphate; the latter colour dyes silk, but cannot be fixed on mordanted cotton. These colour reactions distinguish the aloins of Natal aloes from barbaloin. G. T. M.

**Brazilin and Hæmatoxylin.** By JOSEF HERZIG (*Monatsh.*, 1899, 20, 461—466. Compare this vol., i, 381).—The author criticises the conclusions of Feuerstein and v. Kostanecki (this vol., i, 538), and of Gilbody and Perkin (*Proc.*, 1899, 15, 75), with regard to the formulæ of brazilin and hæmatoxylin. R. H. P.

**Gossypol, a Constituent of Cotton-seeds.** By LEO MARCHLEWSKI (*J. pr. Chem.*, 1899, 60, 84—90).—When the phenolic constituents of cotton-seed oil are purified by repeated fractionation from acetic acid solution, a crystalline product is obtained which can be further purified by crystallisation from a mixture of alcohol and dilute acetic acid; this substance, to which the name of *gossypol* is given, has a composition corresponding fairly well with that required for the formula  $C_{13}H_{14}O_4$ . Gossypol crystallises in glistening, golden scales, melts at  $188^\circ$ , dissolves readily in alcohol, benzene, chloroform, ether, acetone, or acetic acid, but not in water. Sulphuric acid dissolves it with a beautiful, cherry-red coloration, similar to that observed with impure cotton-oils. Alkalis give a yellow solution, which soon becomes violet and then gradually loses its colour; the violet colour is developed immediately when hydrogen peroxide is added to the alkaline solution. Alkaline solutions of gossypol reduce both Fehling's solution and ammoniacal silver nitrate. An alcoholic solu-

tion gives a dark green coloration with ferric chloride, which becomes dark reddish-brown on adding alkalis. The acetyl and benzoyl derivatives are very soluble in organic solvents, and were not obtained in crystalline form; bromine and nitric acid also act on gossypol, but definite products were not isolated. Gossypol is not a glucoside. An analysis of the lead salt indicates the presence of two hydroxyl groups. Gossypol gives a grey shade with iron mordants. T. M. L.

**Fatty Oil of Quince Seeds.** By ROBERT HERRMANN (*Arch. Pharm.*, 1899, 237, 358—368).—Seeds of the quince (*Cydonia vulgaris*) were ground, dried carefully, and extracted with ether, chloroform, or light petroleum; fresh seeds yielded 15.3 per cent. of oil. The oil was yellow and had a faint odour of oil of almonds; it had a solidification point  $-13.5^{\circ}$ , sp. gr. 0.922 at  $15^{\circ}$ , solubility 4.15 parts in 100 of 95 per cent. alcohol, index of refraction 1.47248 for green, 1.47292 for red, viscosity 16.4 at  $17^{\circ}$  (by Schubler's method, comparing its velocity of efflux with that of water); it was optically inactive and showed obscure absorption bands in the blue and violet. 1 gram neutralised 31.7 milligrams KOH in the cold ("acid number"), 181.7 on heating ("Koettstorfer's" or "saponification number"); 5 grams contained volatile acids soluble in water sufficient to neutralise 0.508 c.c.  $N/10$  KOH solution ("Reichert-Meissl number"); it contained 95.2 per cent. of fatty acids insoluble in water ("Hegner's number"), and united with 113 per cent. of iodine ("Hübl's iodine number").

By hydrolysis of the oil with lead oxide, glycerol was obtained to the extent of 4.1 per cent. A larger quantity of the oil was hydrolysed with caustic soda, and the acids converted into calcium salts, which were then treated with ether. From the calcium salt soluble in ether, a liquid acid was obtained, and purified by conversion into its ethylic salt and fractional distillation of the latter. This acid has a sp. gr. 0.8931 and composition  $\text{OH}\cdot\text{C}_{17}\text{H}_{32}\cdot\text{COOH}$ ; its ethylic salt boils at  $223\text{--}226^{\circ}$  under 7.5 mm. pressure; an anhydrous barium salt, melting at  $79^{\circ}$ , and a monacetyl derivative were prepared; a dibromide,  $\text{C}_{18}\text{N}_{34}\text{O}_3\text{Br}_2$ , was also prepared, and the acid was found to darken in the air, absorbing oxygen. From the calcium salt insoluble in ether, a mixture of solid acids was obtained from which two were separated by crystallisation from 70 per cent. alcohol; these were myristic acid, the main product, and a small amount of an acid which melts at  $42^{\circ}$ , contains C 75.1 and H 12.1 per cent., and is possibly an isomeride of pentadecylic acid. C. F. B.

**Pectin from Quince.** By JAVILLIER (*J. Pharm.*, 1899, [vi], 9, 163—166 and 513—515).—This pectin is strongly dextrorotatory,  $[\alpha]_D = 188.2^{\circ}$ . On hydrolysis with dilute sulphuric acid, it yields arabinose; when treated with nitric acid, it gives mucic acid, and with diastase from germinated barley it behaves exactly like the pectin obtained from gentian and the gooseberry (Bourquelot and Hérissé, *Abstr.*, 1898, i, 607; this vol., i, 653). H. R. LE S.

**Chlorophyll.** By LEO MARCHLEWSKI (*J. pr. Chem.*, 1899, 60, 91—95).—A controversial reply to Kohl (this vol., i, 228).

T. M. L.



**Action of Ethylic Diazoacetate on Pyrroline, 1-Methylpyrroline and some Indoles.** By ANTONIO PICCININI (*Gazzetta*, 1899, 29, i, 363—371).—1-Methylpyrrolylacetic acid,  $C_4NH_3Me \cdot CH_2 \cdot COOH$ , obtained by hydrolysing the product formed by the action of ethylic diazoacetate on 1-methylpyrroline or pyrroline, crystallises from light petroleum in colourless leaflets with a nacreous lustre, and melts at  $113-114^\circ$ ; it is very soluble in water, alcohol, or ether, slightly so in cold light petroleum, and tends to become red in the air. It does not give the pyrroline reaction with isatin, nor does it colour cold concentrated sulphuric acid, but gives immediately an intense red coloration to a pine shaving moistened with hydrochloric acid. The salts formed with the alkali and alkaline-earth metals are very soluble in water; the lead salt forms a white precipitate, and the silver salt colourless, very slightly soluble flocks which change rapidly even in the cold, and when suspended in water and heated are instantly reduced; the mercury salt is deposited as a bulky, colourless precipitate which becomes red, slowly in the cold and more rapidly on heating.

1'-Methylindole-3'-acetic acid,  $MeN \langle \begin{smallmatrix} CH \\ C_6H_4 \end{smallmatrix} \rangle C \cdot CH_2 \cdot COOH$ , prepared from 1'-methylindole and ethylic diazoacetate, forms colourless prisms melting at  $128-129^\circ$ , and is very soluble in benzene or alcohol, less so in boiling water, and only very slightly in light petroleum. The silver salt,  $C_{11}H_{10}NO_2Ag$ , forms a colourless, microcrystalline precipitate readily decomposed by heating, and the picrate is deposited in garnet-red, silky needles melting at  $173-174^\circ$ . On heating the acid at  $200-220^\circ$ , it is converted quantitatively into 1':3'-dimethylindole, carbonic anhydride being eliminated.

2'-Methylindole and ethylic diazoacetate give rise to the 2'-methylindole-3'-acetic acid, melting at  $204^\circ$ , obtained by Fischer (*Abstr.*, 1887, 806) from the phenylhydrazone of lævulinic acid. T. H. P.

**Action of Benzylideneaniline on Pyruvic Acid and its Ethylic Salt.** By KARL GARZAROLLI-THURNLACKH (*Monatsh.*, 1899, 20, 480—487).—The principal product of the action of benzylideneaniline on pyruvic acid or on its ethylic salt is the compound  $C_{22}H_{18}N_2O$ , first obtained by Doebner (*Abstr.*, 1887, 504) by the action of aniline on a mixture of pyruvic acid and benzaldehyde; this the author regards as the 4-anil of 1:2-diphenyl-4:5-diketotetrahydropyrroline. It is only when the reaction occurs in dilute solution that small quantities of diphenyldiketodihydropyrroline are formed (compare Schiff, *Abstr.*, 1898, i, 490). R. H. P.

**Action of Hydrazine Hydrate on Acenaphthenequinone.** By LUDWIG BEREND and JOACHIM HERMS (*J. pr. Chem.*, 1899, [ii], 60, 1—25. Compare Curtius and Thun, *Abstr.*, 1891, 1355).—Perinaphthoylhydrazimethylene,  $\begin{smallmatrix} CO- \\ C_{10}H_6 \end{smallmatrix} \rangle C \langle \begin{smallmatrix} NH \\ NH \end{smallmatrix}$ , produced by the action of hydrazine hydrate on acenaphthenequinone, melts at  $140^\circ$ , and gives off nitrogen when heated to  $165^\circ$ . It crystallises from dilute alcohol in needles of a yellow to brown colour, dissolves readily in hot alcohol and in benzene, ether, or chloroform, but less readily in hot water,

from which it separates unchanged on cooling. A yellow substance which is insoluble in alcohol and does not melt at  $270^{\circ}$  is also produced in the reaction. *Perinaphthoylmethylenemetanitroisobenzalazine*,

$\text{CO} \begin{array}{c} \diagup \\ \text{C}_{10}\text{H}_6 \end{array} \text{C} \begin{array}{c} \text{N} \\ \diagdown \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , produced by condensation of the

hydrazimethylene with metanitrobenzaldehyde, crystallises from nitrobenzene in microscopic, straw-yellow needles, melts and decomposes at  $253^{\circ}$ , dissolves to some extent in boiling chloroform, but not in alcohol or ether. *Perinaphthoylazomethylene*, prepared by oxidising the hydrazo-compound with mercuric oxide, separates from light petroleum in orange to reddish-yellow needles and fan-shaped crystals, melts at  $79-80^{\circ}$ , and loses nitrogen at  $120^{\circ}$ ; it dissolves easily in alcohol, ether, chloroform, benzene, or acetic acid, less readily in light petroleum, and is quite insoluble in water; it explodes when mixed with concentrated sulphuric acid, or when rapidly heated above the

melting point. *Perinaphthoyldibromomethylene*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CO} \\ | \\ \text{CBr}_2 \end{array}$ , separates

from light petroleum in stout prisms and rhombic crystals, and melts at  $160-161^{\circ}$ . *Perinaphthylenehydrazimethylenemetanitroisobenzalazine* (1),

$\begin{array}{c} \text{NH} \\ | \\ \text{NH} \end{array} \text{C} \begin{array}{c} \text{C}_{10}\text{H}_6 \end{array} \text{C} \begin{array}{c} \text{N} \\ | \\ \text{N} \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , prepared by the

action of hydrazine hydrate on the azine described above, crystallises in yellow tablets and melts at  $215-216^{\circ}$  with liberation of nitrogen.

*Perinaphthylenedihydrazimethylene*,  $\begin{array}{c} \text{NH} \\ | \\ \text{NH} \end{array} \text{C} \begin{array}{c} \text{C}_{10}\text{H}_6 \end{array} \text{C} \begin{array}{c} \text{NH} \\ | \\ \text{NH} \end{array}$ , ob-

tained by the action of hydrazine hydrate on the hydrazimethylene derivative, crystallises from dilute alcohol in yellow needles, melts at  $192^{\circ}$ , dissolves readily in hot alcohol or chloroform, less readily in ether or hot water, and is insoluble in cold water. *Perinaphthylenedimetanitroisobenzalazine* (2),

$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{N} \\ | \\ \text{N} \end{array} \text{C} \begin{array}{c} \text{C}_{10}\text{H}_6 \end{array} \text{C} \begin{array}{c} \text{N} \\ | \\ \text{N} \end{array} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ ,

crystallises from chloroform in glistening, hexagonal tablets and prisms, melts at  $246^{\circ}$ , dissolves readily in hot nitrobenzene, and slightly in boiling chloroform, but not at all in alcohol or ether.

*Perinaphthoylmonochloromethylene*,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{CO} \\ | \\ \text{CHCl} \end{array}$ , prepared by the action of hydrogen chloride on perinaphthoylazomethylene, crystallises from chloroform in microscopic, colourless needles, and melts at  $109-110^{\circ}$ .

The paper contains a summary of previous work on the action of hydrazine hydrate on aldehydes and ketones, and a comparison between the behaviour of acenaphthenequinone and benzil towards this agent (Curtius and Thun, *loc. cit.*). T. M. L.

**Paratolylpseudazimidoquinoline.** By CONRAD WILLGERODT and HEINRICH DAUNER (*J. pr. Chem.*, 1899, 60, 72-79).—*Paratolyl-*

*pseudazimidonitrobenzene*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N} \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_3\cdot\text{NO}_2$ , prepared by the action of sodium hydrogen carbonate on paratolylhydrazine and  $\alpha$ -dinitrochlorobenzene in boiling alcoholic solution, crystallises from alcohol in yellow needles, and melts at  $165\text{--}166^\circ$ . *Paratolylpseudazimidoamidobenzene* crystallises from alcohol in greenish needles and melts at  $212\text{--}213^\circ$ .

*Paratolylpseudazimidoquinoline*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N} \begin{smallmatrix} \text{N} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} \text{C}_9\text{NH}_5$ , [ $\text{N} : \text{N} = 3 : 4$  or  $2 : 3$ ], melts at  $184^\circ$ , crystallises from alcohol in yellow needles, dissolves fairly readily in ether or chloroform, and to some extent in hot water or acetic acid. The *hydrochloride*,  $\text{C}_{16}\text{H}_{12}\text{N}_4\cdot\text{HCl}$ , crystallises from alcohol in yellowish-white, glistening needles, and melts and decomposes at  $224^\circ$ ; the *nitrate* separates from alcohol in short, brownish needles and melts at  $192^\circ$ ; the *sulphate* crystallises from alcohol in brown needles and melts and decomposes at  $248^\circ$ . The *dichromate* crystallises in splendid, orange-yellow needles, but blackens when exposed to light. The *acetate* forms grey, glistening, pointed leaflets and melts at  $180^\circ$ . The *platinochloride*,  $(\text{C}_{16}\text{H}_{12}\text{N}_4)_2\cdot\text{H}_2\text{PtCl}_6$ , and the *mercurichloride* crystallise in microscopic needles. The *methiodide* crystallises from hot water in splendid, golden-yellow needles and melts at  $268^\circ$ ; the *ethiodide* crystallises in flat, golden needles. The *ethobromide* melts at  $203^\circ$ , and is only very slightly soluble in hot water, but crystallises from alcohol in short, grey leaflets. The *methochloride* separates from water in a white, crystalline mass, dissolves readily in alcohol, and melts at  $225^\circ$ ; the *ethochloride* is extremely soluble in alcohol and water. The *methiodichromate*,  $(\text{C}_{16}\text{H}_{12}\text{N}_2\text{Me})_2\text{Cr}_2\text{O}_7$ , crystallises from water in fine, orange-yellow needles and dissolves readily in alcohol; its temperature of decomposition is very high. T. M. L.

**Diazoles from Carbazinic Acids.** By MAX BUSCH (*J. pr. Chem.*, 1899, [ii], 60, 25–55).—The dithiocarbazinic acids,  $\text{R}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{SH}$  or  $\text{R}\cdot\text{NH}\cdot\text{N}:\text{C}(\text{SH})_2$ , as well as their metallic and ethereal salts, condense with various substances to form ring compounds containing two atoms of nitrogen. Carbon bisulphide gives dithiodiazolonethiols,  $\text{R}\cdot\text{N} \begin{smallmatrix} \text{N}=\text{C} \\ \diagup \diagdown \\ \text{CS}\cdot\text{S} \end{smallmatrix} \text{SK}$ ; carbonyl chloride gives thiodiazolonethiols,  $\text{R}\cdot\text{N} \begin{smallmatrix} \text{N}=\text{C} \\ \diagup \diagdown \\ \text{CO}\cdot\text{S} \end{smallmatrix} \text{SH}$ ; aldehydes and certain ketones give thiodiazolinethiols,  $\text{R}\cdot\text{N} \begin{smallmatrix} \text{N}=\text{C} \\ \diagup \diagdown \\ \text{CR}^1\text{R}^{11}\cdot\text{S} \end{smallmatrix} \text{SH}$ , which can also be prepared by reducing the dithiodiazolonethiols; acid chlorides give isodithiodiazolones,  $\text{R}\cdot\text{N} \begin{smallmatrix} \text{N}=\text{CS} \\ \diagup \diagdown \\ \text{CR}^1\cdot\text{S} \end{smallmatrix}$ . The condensation products of carbon bisulphide with dithiocarbazinic acid, and with methyl dithiocarbazinic acid are described below, the other series of compounds being described in a later paper.

I [By E. ZIEGELE. Compare Curtius and Heidenreich, *Abstr.*, 1894, i, 166.]—The *dimethylic ether* of *thiodiazoledithiol*,  $\text{S} \begin{smallmatrix} \text{C}(\text{SMe})\cdot\text{N} \\ \diagup \diagdown \\ \text{C}(\text{SMe})\cdot\text{N} \end{smallmatrix}$ ,

crystallises from benzene in long, glistening needles, melts at  $136^{\circ}$ , and dissolves readily in the ordinary organic solvents. When oxidised

with iodine, the dithiol yields a *bisulphide*,  $S_2\left(C\begin{smallmatrix} N\cdot N \\ \diagup \diagdown \\ S\cdot C\cdot SH \end{smallmatrix}\right)_2$ , which separates from dilute methylic alcohol in lemon-yellow, glistening crystals, melts at  $175^{\circ}$ , and dissolves readily in boiling ethylic or methylic alcohol, or in ethylic acetate. Ferric chloride gives the same bisulphide, together with a *polysulphide*,  $(C_2N_2S_3)_x$ , which was obtained as an insoluble, white powder melting at  $207^{\circ}$  to a yellow oil, and was reduced again to the dithiol by alcoholic potash or alcoholic ammonia. The *potassium* salt of the bisulphide,  $C_4N_4S_6K_2$ , forms lemon-yellow needles and melts at  $205^{\circ}$ ; the action of alcoholic potash on the bisulphide at the ordinary temperature instead of at that of a freezing mixture, however, brings about the reduction of the bisulphide to the potassium salt of the dithiol. The *dibenzyllic ether*,  $C_{18}H_{14}N_4S_6$ , forms white, felted needles and melts at  $109^{\circ}$ . When oxidised with potassium permanganate, the dithiol gives *potassium thiodiazoledisulphonate*,  $S\begin{smallmatrix} C(SO_3K):N \\ \diagup \diagdown \\ C(SO_3K):N \end{smallmatrix}$ , which crystallises from water in large, glistening prisms. It was not found possible to produce either thiodiazole,  $S\begin{smallmatrix} CH:N \\ \diagup \diagdown \\ CH:N \end{smallmatrix}$ , or dihydroxythiodiazole,  $S\begin{smallmatrix} C(OH):N \\ \diagup \diagdown \\ C(OH):N \end{smallmatrix}$ , by elimination of the sulphonic groups, but hydrolysis with hydrochloric acid gave *potassium oxythiodiazoledisulphonate*,  $S\begin{smallmatrix} C(OH)=N \\ \diagup \diagdown \\ C(SO_3K):N \end{smallmatrix}$ .

The action of ammonia on the bisulphide of thiodiazoledithiol appears to give rise to the ammonium salts of the dithiol and of thiodiazoledithiolsulphamine,  $S\begin{smallmatrix} C(SH)=N \\ \diagup \diagdown \\ C(S\cdot NH_2):N \end{smallmatrix}$ , but these could not be isolated. The dibenzyllic ether of the bisulphide acts similarly, but the hydrosulphamine derivative could not be isolated; the *monobenzyllic ether*,  $S\begin{smallmatrix} C(SH)=N \\ \diagup \diagdown \\ C(S\cdot CH_2Ph):N \end{smallmatrix}$ , which is formed as the other product of the action, melts at  $131^{\circ}$ , dissolves readily in alkalis, and in alcohol, chloroform, ether, or benzene, and crystallises well from dilute alcohol.

The action of aniline on the bisulphide gives rise to the original bisulphide together with *amidobenzene-thio-thiodiazoledithiol* (mercapto-thiodiazolediamidophenylsulphide),  $SH\cdot\overset{N\cdot N}{\underset{||}{C}}\cdot S\begin{smallmatrix} \diagup \diagdown \\ C\cdot S\cdot C_6H_4\cdot NH_2 \end{smallmatrix}$ ; this crystallises from 50 per cent. alcohol in colourless needles, melts at  $187^{\circ}$ , dissolves readily in alcohol, ether, or hot water, but only slightly in chloroform or benzene; it smells of an isonitrile when heated with chloroform and alcoholic potash, gives a diazo-compound with nitrous acid, and possesses both acid and basic properties. The *hydrochloride* crystallises in colourless needles and melts at  $206^{\circ}$ . The *diazochloride* melts with frothing at  $133^{\circ}$  and condenses with  $\beta$ -naphthol to a red dye which melts at  $222^{\circ}$ . It is probable that the first product of the action of aniline on the bisulphide is the hydrosulphamine

derivative,  $\text{SH} \cdot \overset{\text{N} \cdot \text{N}}{\underset{\text{S}}{\text{C}}} > \text{C} \cdot \text{S} \cdot \text{NHPh}$ , and that isomeric change subsequently takes place, the radicle ( $\text{C}_2\text{S}_3\text{N}_2\text{H}$ ) being transferred to the para-position relatively to the amido-group.

II [By E. ZIEGELE.]—*Methyldithiodiazolonethiol*,  $\text{NMe} < \overset{\text{N}=\text{C} \cdot \text{SH}}{\underset{\text{CS} \cdot \text{S}}{\text{S}}}$ , forms colourless needles which melt at  $69^\circ$  to a yellow oil. The *methylic* salt separates from dilute alcohol in fine, glistening, flat needles, melts at  $88^\circ$ , and dissolves easily in most solvents; like other organic sulphides, it forms an additive compound with bromine, which crystallises from benzene and melts at  $124^\circ$ . The *benzoyl* derivative melts at  $157^\circ$  and dissolves readily in benzene, chloroform, or absolute alcohol. The *bisulphide* separates from chloroform, on adding alcohol, in glistening, flat, yellowish needles, which soften at  $138^\circ$  and melt at  $141^\circ$ . On oxidation with potassium permanganate, the thiol gives *potassium methyldithiodiazolonesulphonate*,  $\text{C}_3\text{H}_3\text{N}_2\text{S}_2 \cdot \text{SO}_3\text{K}$ , which crystallises in spherical aggregates of slender needles. T. M. L.

**Oxidation of Hydrazoximes. IV.** By GIACOMO PONZIO (*Gazzetta*, 1899, 29, i, 349—357. Compare Abstr., 1898, i, 386, and this vol., i, 717).

—*Phenyl-2-methyl-3-ethyl-1:2-oxypyrrro-1:4-diazole*,  $\text{O} < \overset{\text{CMe} - \text{CEt}}{\underset{\text{N} \cdot \text{NPh} \cdot \text{N}}{\text{N}}}$ , obtained by oxidising  $\beta\alpha$ -acetylpropionylhydrazoxime in chloroform solution by means of mercuric oxide, crystallises from light petroleum in faintly yellow, glistening prisms melting at  $43$ – $44^\circ$ , and dissolves in the cold in all ordinary organic solvents except light petroleum, and also to a slight extent in hot water. Its *hydrochloride*,  $\text{C}_{11}\text{H}_{13}\text{N}_3\text{O} \cdot \text{HCl}$ , crystallises in white prisms, is decomposed immediately by water with the liberation of the base, and slowly loses hydrogen chloride when left in the air. When the base is reduced in concentrated hydrochloric acid solution by means of granulated zinc, methylethylphenylosotriazole is obtained. The *nitro*-derivative,  $\text{C}_2\text{ON}_3\text{MeEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , prepared by dissolving the phenylmethyl-ethyloxypyrrrodiazole in cold concentrated nitric acid, crystallises from alcohol in yellowish plates melting at  $131^\circ$ , and is soluble in benzene, chloroform, or hot alcohol, but dissolves only slightly in ether, light petroleum, or cold alcohol. On reduction in alcoholic solution with zinc and hydrochloric acid, it forms *amidophenylmethyl-ethylsotriazole*,  $\text{C}_2\text{N}_3\text{MeEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , which melts at  $95$ – $96^\circ$ , and is very soluble in ether, benzene, or chloroform, but almost insoluble in light petroleum.

*Phenyl-2-ethyl-3-methyl-1:2-oxypyrrro-1:4-diazole*,  $\text{O} < \overset{\text{CEt} - \text{CMe}}{\underset{\text{N} \cdot \text{NPh} \cdot \text{N}}{\text{N}}}$ , prepared from  $\alpha\beta$ -acetylpropionylhydrazoxime, is a faintly yellow liquid which is heavier than water, does not solidify even at low temperatures, and cannot be distilled unchanged at a low pressure. It is slightly soluble in water, and mixes with all ordinary organic solvents except light petroleum. It is non-volatile in steam. The *hydrochloride*,  $\text{C}_2\text{ON}_3\text{MeEtPh} \cdot \text{HCl}$ , slowly loses hydrogen chloride

when left exposed to the air, and in contact with water is decomposed with liberation of the base. The *nitro*-derivative,  $C_2ON_3MeEt \cdot C_6H_4 \cdot NO_2$ , crystallises from alcohol in glistening, yellowish plates melting at  $156-157^\circ$ ; it is slightly soluble in ether or light petroleum, more so in chloroform or benzene, and when reduced in alcoholic solution by means of zinc and hydrochloric acid yields the amido-compound melting at  $95^\circ$ .

By reducing with zinc and hydrochloric acid the product of the reaction of mercuric oxide on either  $\alpha\beta$ - or  $\beta\alpha$ -acetylpropionylhydrazoxime, methylethylphenylosotriazole,  $C_2N_3MeEtPh$ , boiling at  $282-283^\circ$  under 751.1 mm. pressure is obtained; von Pechmann (Abstr., 1891, 1110) gives its boiling point as about  $270^\circ$ . Its *nitro*-derivative,  $C_2N_3MeEt \cdot C_6H_4 \cdot NO_2$ , crystallises from alcohol in long, slightly yellowish needles melting at  $127-128^\circ$ ; it is soluble in chloroform, but only slightly so in ether or light petroleum. The *chloro*-derivative,  $C_2N_3MeEt \cdot C_6H_4Cl$ , crystallises from alcohol in very thin, white needles melting at  $81^\circ$ , is soluble in cold ether, chloroform, or light petroleum, and is volatile in steam; on boiling with nitric acid of sp. gr. 1.52 it is completely converted into nitromethylethylphenylosotriazole melting at  $127-128^\circ$ , but with ordinary concentrated nitric acid it yields *chloronitromethylethylphenylosotriazole*,  $C_2N_3MeEt \cdot C_6H_3Cl \cdot NO_2$ , which crystallises from alcohol in small, faintly yellowish prisms melting at  $86-87^\circ$ , and dissolves only slightly in alcohol or light petroleum, but more readily in ether or benzene. *Bromomethylethylphenylosotriazole*,  $C_2N_3MeEt \cdot C_6H_4Br$ , crystallises from alcohol in glistening white needles melting at  $107-108^\circ$ , and dissolves in the ordinary organic solvents. T. H. P.

**Metanitroguanazylmethane and Allied Compounds.** By EDGAR WEDEKIND [and S. BRONSTEIN] (*Annalen*, 1899, 307, 293-305).—The *nitrate* of amidoguanidinepyruvic acid,  $C_4H_8N_4O_2 \cdot HNO_3$ , obtained by mixing cold, concentrated, aqueous solutions of amidoguanidine nitrate and pyruvic acid, crystallises in colourless needles containing  $\frac{1}{2}H_2O$ , which is removed at  $120^\circ$ ; the salt melts at  $206^\circ$ . The free *base*, which is trimeric, separates from hot water as a colourless, crystalline powder, dissolving with difficulty in organic media excepting glacial acetic acid; it blackens at about  $340^\circ$  and decomposes at  $350-360^\circ$  without fusion. The *silver* salt,  $C_4H_6N_4O_2Ag_2$ , detonates when heated, and dissolves in warm ammonia, forming a mirror; the *hydrochloride* crystallises in lustrous leaflets and melts to a red liquid at  $245-246^\circ$ .

*Metanitroguanazylmethane*,  $NO_2 \cdot C_6H_4 \cdot N:N \cdot CMe:N \cdot NH \cdot C(NH_2):NH$ , obtained by adding diazotised metanitriline to an ice-cold solution of amidoguanidinepyruvic acid (compare Wedekind, Abstr., 1897, i, 241), crystallises from alcohol in red needles and prisms melting at  $222^\circ$ ; it is insoluble in water and petroleum, but forms deep red solutions in other media. Reduction with stannous chloride and hydrochloric acid changes the red colour to yellow; oxidation with nitric acid gives rise to a *compound* which melts at  $180^\circ$ .

The *compound*  $C_9H_{13}N_7O_6$ , obtained instead of metanitroguanazyl-

formic acid when diazotised metanitriline is added to amidoguanidine-glyoxylic acid, crystallises from glacial acetic acid in red needles and melts at  $172^{\circ}$ .

*Acetophenoneamidoguanidine*,  $\text{CMePh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$ , prepared by heating acetophenone dissolved in alcohol with aqueous amidoguanidine nitrate and caustic potash, crystallises from dilute alcohol in lustrous, colourless leaflets and melts at  $182\cdot5^{\circ}$ ; it is insoluble in petroleum. M. O. F.

**Double Salts of Nicotine Hydrochloride and Cadmium Chloride.** By CHARLES GLASER (*J. Soc. Chem. Ind.*, 1899, 18, 563—564).—When an alcoholic solution of nicotine hydrochloride is added to a large excess of an alcoholic solution of cadmium chloride, the compound  $(\text{C}_{10}\text{H}_{14}\text{N}_2\cdot 2\text{HCl})_3\cdot 7\text{CdCl}_2$  is obtained; this crystallises from alcohol in kidney-shaped masses. If, however, the proportions are reversed, a compound,  $(\text{C}_{10}\text{H}_{14}\text{N}_2\cdot 2\text{HCl})_2\cdot 3\text{CdCl}_2 + 2\text{H}_2\text{O}$ , is obtained which crystallises from 50 per cent. alcohol in radiate clusters of fine needles and thin plates. In these compounds, the nitrogen was estimated by the soda-lime method, as the Kjeldahl process yielded only about 68 per cent. of the nitrogen as ammonia. L. DE K.

[**Hyoscyamine from**] *Datura Fastuosa*. By W. P. H. VAN DEN DRIESSEN MAREEUW (*Chem. Centr.*, 1899, i, 539; from *Ned. Tijds. Pharm.*, 1899, 11, 14—19).—The seeds of *Datura fastuosa* contain about 10·9 per cent. of fat and 0·149 of hyoscyamine.

E. W. W.

**Constitution of the Alkaloids of the Pomegranate.** By ANTONIO PICCININI (*Gazzetta*, 1899, 29, i, 408—420).—*Dibenzylidenemethylgranatonine*,  $\text{C}_5\text{NH}_8\text{Me}\langle\begin{smallmatrix} \text{C}(\text{CHPh}) \\ \text{C}(\text{CHPh}) \end{smallmatrix}\rangle\text{CO}$ , prepared by the action of hydrogen chloride on a mixture of benzaldehyde and a glacial acetic acid solution of methylgranatonine, crystallises from alcohol in small yellow prisms melting at  $200^{\circ}$ ; it is soluble in benzene or methylic alcohol, and with concentrated sulphuric acid gives an orange-red coloration.

*Di-isonitrosomethylgranatonine*,  $\text{C}_5\text{NH}_8\text{Me}\langle\begin{smallmatrix} \text{C}(\text{N}\cdot\text{OH}) \\ \text{C}(\text{N}\cdot\text{OH}) \end{smallmatrix}\rangle\text{CO}$ , obtained by the action of amyl nitrite on methylgranatonine, crystallises from boiling water in sulphur-yellow, acicular prisms, which deflagrate when heated on platinum foil; with a trace of ferrous sulphate in aqueous solution, it gives an intense green coloration, but it has no action on cold ferric chloride. The *hydrochloride*,  $\text{C}_9\text{H}_{13}\text{O}_3\text{N}_3\cdot\text{HCl}$ , crystallises from dilute alcohol in yellowish prisms decomposing at  $240\text{--}250^{\circ}$  with evolution of gas; it is slightly soluble in cold, and more so in hot water.

*Granatic acid*,  $\text{COOH}\cdot\text{C}_5\text{NH}_9\cdot\text{CH}_2\cdot\text{COOH}$ , formed when granatoline is oxidised by boiling with a large excess of a sulphuric acid solution of chromic acid, crystallises in colourless prisms, softening at  $265^{\circ}$ , and melting at  $270^{\circ}$ . If only a small quantity of the oxidising mixture is employed at a temperature of  $50\text{--}70^{\circ}$ , granatonine is produced.

*Granatonine*,  $\text{C}_5\text{NH}_9\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CO}$ , forms small, colourless crystals

melting at about  $128^{\circ}$ . It gives a colourless, crystalline *hydrochloride* and a pale yellow, unstable *aurichloride*, which dissolves in boiling water with partial reduction; the *platinochloride*,  $(C_8H_{13}NO)_2 \cdot H_2PtCl_6 + 2H_2O$ , separates in large, yellow, crystalline leaflets melting, with previous softening, at about  $230^{\circ}$ , dissolves slightly in cold, and more so in hot water, and loses its water of crystallisation in a desiccator over sulphuric acid. *Nitrosogranatonine*,  $NO \cdot C_8H_{12}NO$ , separates from a boiling, aqueous solution in colourless leaflets melting at  $199^{\circ}$ . *Dibenzylidenegranatonine*,  $C_{22}H_{21}NO$ , separates from alcohol in small, sparkling, yellow crystals melting at  $182-183^{\circ}$ ; it is readily soluble in benzene or boiling alcohol, slightly so in ether, insoluble in water, and with concentrated sulphuric acid gives an orange-red solution.

By the action of mercuric acetate on granatic acid, a pyridine-carboxylic acid is obtained, and when the product is distilled with barium hydroxide,  $\alpha$ -methylpyridine is formed.

The author is of opinion that the characteristic chain of tropinone,  $-CH_2 \cdot CO \cdot CH_2-$ , is also present in methylgranatonine. T. H. P.

[NOTE BY ABTRACTOR.—In a paper by Ciamician and Silber (Abstr., 1896, i, 397), a compound termed granatic acid is described; it is obtained by the oxidation of methylgranatoline, and has the composition  $C_9H_{15}NO_4$ , whilst the author's granatic acid has the formula  $C_8H_{13}NO_4$ . T. H. P.]

**Study of an Oxyptomaine.** By WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1899, 129, 109—110).—The following compounds of the oxyptomaine or collidone,  $C_8H_{11}NO$  (Abstr., 1898, i, 455), are described. The *platinochloride*,  $(C_8H_{11}NO)_2 \cdot H_2PtCl_6 + H_2O$ , is crystalline, and is completely decomposed by hot, but not by cold, water. The *hydrobromide*,  $C_8H_{11}NO \cdot HBr$ , is very similar to the hydrochloride, and forms deliquescent, elongated plates, which are easily soluble in cold, but rapidly decomposed by boiling, water. The *aurichloride*,  $C_8H_{11}NO \cdot HAuCl_4$ , is yellow, and in aqueous solution is decomposed on evaporation on the water-bath. The *mercurichloride*,  $(C_8H_{11}NO \cdot HCl)_2 \cdot 3HgCl_2$ , a white precipitate, is insoluble in cold, but slightly soluble in warm, water, and is decomposed on prolonged boiling of its aqueous solution. H. R. LE S.

**Action of Iodine on Bilirubin.** By ADOLF JOLLES (*Monatsh.*, 1899, 20, 282—306, and *J. pr. Chem.*, 1899, [ii], 59, 308—319).—The author maintains that, contrary to the view taken by Thudichum (Abstr., 1896, i, 516), the action of iodine in very dilute solution on bilirubin is essentially one of oxidation, and not of substitution, the product being biliverdin.

When bilirubin dissolved in chloroform is treated with a dilute solution of iodine in alcohol, or, better, with Hübl's solution, the same coloured products are obtained as when nitric acid is used as the oxidising agent. The extent of the oxidation depends on the concentration of the solutions, the duration of the action, and the miscibility of the liquids used as solvents. It is also necessary to operate on small quantities at a time, 20—50 milligrams of bilirubin, dissolved in 50—80 c.c. of chloroform, being oxidised with *N*/10 alcoholic solution of iodine, or better, with *N*/10 Hübl's solution. The production of



biliverdin is accomplished by using the materials in the proportions indicated by the equation  $C_{16}H_{18}N_2O_3 + 2I + H_2O = C_{16}H_{18}N_2O_4 + 2HI$ , the mixture being well shaken and left for some time; the solution of the product is finally washed with very dilute hydrochloric acid until hydriodic acid can no longer be detected in the wash-liquors.

Biliverdin,  $C_{16}H_{18}N_2O_4$ , is a green, amorphous substance, and resembles the compound obtained by Maly's method (*Annalen*, 1874, 175, 82) in its solubility in various liquids. The solution in alcohol, rendered slightly acid with mineral acids, gives with acids a bluish-green, and with alkalis a brownish-green, coloration, which gradually fades. On adding ammoniacal alcoholic zinc chloride to the alcoholic solution, a reddish-brown liquid with a green fluorescence is obtained, and when zinc dust is added to the solution of the substance in sulphuric or alcoholic hydrochloric acid, the colour changes to yellowish-green and finally to yellow. When chlorine water is passed down the side of a vessel containing a solution of the substance in alcoholic hydrochloric acid, a blue ring is formed at the bottom of the vessel, the supernatant layer being successively violet, red, and yellow; on adding more chlorine water, the whole becomes yellow, and finally colourless. Potassium permanganate and hydrogen peroxide produce similar colour phenomena.

The spectra given by the author (Abstr., 1894, ii, 466) for bilirubin and biliverdin differ from those of the substances obtained by Maly's method, inasmuch as they exhibit bands due to the presence of an impurity in the substance purchased as pure from a manufacturing firm. Pure biliverdin in alkaline solution shows no absorption bands, but the acidified solution shows a weak band at about D, and one more strongly pronounced between  $E\frac{2}{3}F$  and F.

If bilirubin, dissolved in chloroform, is left for some days with excess of Hübl's solution, an amount of the latter equivalent to three atomic proportions of oxygen is used up. The product, for which the author proposes the term *bilixanthin*, may be isolated by washing the chloroform solution with water acidified with hydrochloric acid, the solvent being subsequently removed by careful evaporation. Bilixanthin,  $C_{16}H_{18}N_2O_6$ , does not exhibit any tendency to crystallise, and is possibly identical with "uroxanthin," a substance obtained by the author from urine. It dissolves in alcohol or chloroform, is soluble for the most part in ether and more so in amylic alcohol, but is insoluble in carbon bisulphide; it is insoluble in the common mineral acids, and the presence of these does not influence its solubility in alcohol; it dissolves for the most part in solutions of alkalis and alkali carbonates. An alcoholic solution of bilixanthin is not altered on addition of hydrochloric acid and zinc dust, or on treatment with hydrogen sulphide, and it does not exhibit any fluorescence with an ammoniacal solution of zinc chloride.

Bilirubin in urine may be fairly accurately estimated by taking advantage of the fact that it is converted into a green colouring matter by means of an alcoholic solution of iodine, two atomic proportions of the latter being required. The method consists in extracting the biliary colouring matters with chloroform, shaking the latter with a known quantity of iodine solution for some minutes, and finally

titrating the excess of halogen with thiosulphate ; the description of the details, however, is lengthy and unsuitable for abstraction.

A. L.

**Solvent Power of Pepsin.** By JEAN EFFRONT (*Bull. Soc. Chim.*, 1899, [iii], 21, 683—691).—The solvent power of pepsin, which should be carefully distinguished from its hydrolytic or peptonising properties, increases with the acidity of the medium until a maximum is reached, after which a decrease is observed. Hydrochloric acid is considerably more effective than sulphuric acid, but the amount required to bring about the best results depends on the state of division of the proteid, and on other circumstances. The solvent power of different samples of pepsin may be compared by measuring the time required to render transparent a definite volume of a 4 per cent. emulsion of albumin ; a detailed description of this method is given in the paper. The rate of solution is largely dependent on the temperature, being most rapid at 65° in the case of neutral solutions, whilst in the presence of 0.15, 0.3, and 0.4 per cent. of hydrochloric acid, the most favourable temperatures are 65°, 55°, and 50° respectively. In each case, it is found that solution takes place most rapidly at a temperature approaching that at which, under the given conditions of acidity, destruction of the ferment occurs. Peptic solution is retarded by the addition of metallic salts, and the effect of a number of these was examined quantitatively. Sulphates, and particularly ammonium sulphate, are most active in this respect. Caffeine, fatty acids, and alcohols are without influence.

N. L.

**Action of Trypsin on the less Complex Chemical Compounds.** By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, 27, 540—556).—In view of Kossel's work on the action of trypsin on protamine, and in the hope that some light might be shed on the constitution of the proteid molecule, a number of organic compounds such as phenetol, ethylaniline, diphenylcarbamide, acetanilide, orthacetamidobenzoic acid, and salol, were subjected to the action of the tryptic ferment. The results of the experiments were negative, except in the case of para-diacetylamidophenol, which, with powerful solutions of trypsin, gave rise to acetic acid. Nencki and Blank have stated (*Arch. exp. Path. Pharm.*, 20, 377) that hippuric acid is decomposed by trypsin ; this was not confirmed ; possibly the trypsin they used was contaminated with the fat-splitting ferment of the pancreas.

W. D. H.

**Diastatic Functions of Indigo-yielding Plants.** By L. BRÉAUDAT (*Compt. rend.*, 1899, 128, 1478—1480. Compare this vol., i, 232).—The indigotic fermentation of the leaves of *Isatis alpina*, which is brought about by a hydrolytic diastase and an oxydase present in the leaves, is promoted by the presence of ammonia, baryta, magnesia, and the carbonates of the alkali or alkaline-earth metals, either dissolved or in suspension in the fermenting liquor. In presence of acids or neutral salts, no formation of indigo is detected. The alkali only affects the action of the oxydase, the feeble oxidising power of which it increases.

T. H. P.

**Protamines.** By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1899, 26, 588—592. Compare Abstr., 1896, i, 582; 1898, i, 714).—Renewed experiments have shown that histidine is not formed in the hydrolysis of clupeine, salmine, or scombrine with dilute sulphuric acid. Nor does clupeine yield lysine in these circumstances; a substance, which has the composition of an amidovaleric acid and sublimes when heated cautiously, is obtained, however, along with another more soluble substance. And sturine is now found to yield some substances of a similar nature in addition to the three hexon bases, arginine, histidine, and lysine.

Protamines, therefore, must be subdivided into two groups: those of the one group, exemplified by sturine, yield all three hexon bases when hydrolysed; those of the other, namely, clupeine, salmine, and scombrine, yield arginine only. If a protamine nucleus does form the basis of the albumin molecule, it must be one of the sturine type, since the proteids, like sturine, yield all three hexon bases.

C. F. B.

**Preparation and Detection of Lysine.** By ALBRECHT KOSSEL (*Zeit. physiol. Chem.*, 1899, 26, 586—587).—From the products of decomposition of proteids, the bases are precipitated with phosphotungstic acid, the precipitate is decomposed with baryta, from the filtered liquid the histidine and arginine are precipitated with silver sulphate and baryta (Abstr., 1898, i, 715), and the filtrate is evaporated to a syrup and mixed with alcoholic picric acid, when lysine picrate,  $C_6H_4N_2O_2 \cdot C_6H_3N_3O_7$ , separates; this is recrystallised from a small quantity of boiling water. To convert it into the hydrochloride, it is dissolved in dilute hydrochloric acid, the picric acid is removed by extraction with ether, and the liquid is then evaporated to a syrup and mixed with a little hot alcohol, when lysine hydrochloride crystallises out as the mixture cools.

C. F. B.

**Arginine.** By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, 27, 178—215, and 368—369).—Arginine has been prepared from the testicles of salted herrings, and a number of its salts examined. Most of these have been prepared before (Schulze and Steiger, Abstr, 1886, 725; Hedin, Abstr., 1895, i, 160; 1896, i, 193); the hydrochloride however, as crystallised from alcohol, contained  $1H_2O$  (Schulze and Steiger describe it as anhydrous; Hedin, with  $1H_2O$ ), and the copper nitrate compound,  $3\frac{1}{2}H_2O$  ( $3H_2O$ , according to these authors). A crystalline *phosphotungstate*,  $3C_6H_{14}N_4O_2 \cdot 2H_3PO_4 \cdot 24WO_3 + 10H_2O$ , and a *mercurichloride* compound, melting and decomposing at  $186-189^\circ$  are described, apparently for the first time: in the latter, the ratio  $Hg:Cl$  is 1:1, and hence the compound is of the nature of a mercuric derivative of the base. The hydrochloride melts and decomposes at about  $209^\circ$  when anhydrous, the nitrate melts partially and begins to decompose at  $175^\circ$ ; the acid nitrate (with  $2HNO_3$ ) melts and decomposes at  $144.5-145^\circ$ ; the copper nitrate compound melts at  $112-114^\circ$ , or at  $232-234^\circ$  with decomposition when anhydrous; the copper sulphate compound melts at about  $110^\circ$ , and when anhydrous decomposes at  $235-238^\circ$ ; the silver nitrate compound

(with  $\text{AgNO}_3$ ) decomposes at  $164^\circ$ , the acid compound (with  $\text{HNO}_3, \text{AgNO}_3$ ) melts and decomposes at about  $180^\circ$ . The specific rotation,  $[\alpha]_D$ , calculated for the arginine, is about  $12.5^\circ$  for the hydrochloride in aqueous solution, and is raised to about  $25.5^\circ$  by addition of excess of hydrochloric acid, and lowered to about  $11.5^\circ$  by addition of a slight excess of barium hydroxide; for the nitrate, the value is about  $12.5^\circ$ , raised to about  $25.5^\circ$  by the addition of excess of acid (about  $13^\circ$  for the compound with  $\text{HNO}_3, \text{AgNO}_3$ ); for the sulphate  $10.5^\circ$ , raised to  $22.5^\circ$ . A silver derivative of arginine (compare Kossel, Abstr., 1898, i, 715) was precipitated by adding silver nitrate to a solution of one of the silver nitrate compounds, until the ratio  $\text{AgNO}_3 : \text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$  was 2 : 1, and then adding just enough alkali to combine with all the nitric acid present; the resulting compound is amorphous and unstable in daylight; it appears to consist mainly of  $\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2\text{Ag}_2 + \text{H}_2\text{O}$  mixed with a little  $\text{C}_6\text{H}_{11}\text{N}_4\text{O}_2\text{Ag}_3 + \text{H}_2\text{O}$ .

The arginine itself was prepared by boiling the testicles with dilute sulphuric acid (1 : 2) for 8 hours, neutralising with chalk, adding silver nitrate to the concentrated filtrate until a drop gave a brownish precipitate with baryta water, saturating the filtered liquid with baryta water, washing the precipitate of arginine-silver with water, decomposing it with hydrogen sulphide, removing carbonic acid with baryta water, neutralising with nitric acid and adding silver nitrate and ammonia alternately so long as a small quantity of either produced a further precipitate, filtering from the precipitated silver compounds of histidine and thymine, neutralising with nitric acid and evaporating to the crystallising point, purifying the crystals of the silver compound (with  $\text{HNO}_3, \text{AgNO}_3$ ) by recrystallisation from hot water, converting these into arginine-silver, decomposing this with hydrogen sulphide, and evaporating the filtrate to the crystallising point. Arginine decomposes at  $207-207.5^\circ$ , and has the properties of an alkali; for instance, it absorbs carbonic anhydride from the air. Its molecular weight determined by cryoscopic methods, using water as solvent, agrees with that required by the formula  $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$ . The *dibenzoyl* derivative,  $\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2\text{Bz}_2$ , forms needles or tablets belonging to the rhombic system, melts at  $217.5-218^\circ$ , and in its properties shows much resemblance to ornithuric acid.

The discrepancy between the author's polarimetric results and those of Schulze and Steiger is due to the fact that these observers stated the rotation of an aqueous solution of arginine nitrate (of vegetable origin) in degrees of the Ventzke scale, not in angular degrees. This being so, the rotation proves to be practically identical with that of arginine from animal sources, and there is no reason therefore to suspect the existence of two dextrorotatory arginines. C. F. B.

**Thymine.** By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, 27, 292—296).—Thymine, obtained by boiling herrings' testicles with dilute sulphuric acid (preceding abstract), was compared, as regards crystalline form, with that from the thymus and from the milt of the sturgeon (Kossel, Abstr., 1894, i, 156, 631; 1896, ii, 537). The crystals sometimes have a rounded outline, but frequently are bounded by straight lines meeting at  $90^\circ$  or  $45^\circ$ ; they show extinction parallel

to one set of these lines. Some characteristic shapes are figured in the paper.  
C. F. B.

**Chemical Examination of Laben.** By NICOLAS GEORGIADÈS (*J. Pharm.*, 1899, [vi], 9, 519—521).—Laben is produced by the action of a special ferment on the milk of the cow or goat, and is used as a food by the people of Syria. After the introduction of the ferment, the milk coagulates and the lactose is decomposed into carbonic, acetic, and lactic acids, the last two increase in amount until the third day after the introduction of the ferment, when butyric fermentation sets in and the liquid is no longer fit for food. Small quantities of alcohol and glycerol were also found in the liquid. The butyric fermentation is accidental and does not occur, if, after the ferment is introduced, the milk is put into flasks which have been carefully cleaned.  
H. R. LE S.

**Action of Pepsin and Pancreatic Juice on Albumin.** By V. HARLAY (*J. Pharm.*, 1899, [vi], 9, 424—428. Compare this vol., i, 656).—The results confirm the author's statement (*loc. cit.*), that the absence of a turbidity, on the addition of nitric acid to the filtrate from the products of digestion, is no proof that the digestive action is ended. The digestive action of pepsin and pancreatic juice on albumin is quite analogous to that on fibrin, except that pancreatic juice acts much more slowly on the former, and digestion is not complete even after the addition of sodium hydrogen carbonate. The juice of *Russula delica* gave a colour change of red to green with the liquid from the pepsin digestion, and of red to black with that from pancreatic digestion. Tyrosine was found in the liquid from the action of the pancreatic juice on albumin.  
H. R. LE S.

**Two New Reactions of the Products of the Digestive Action of Pepsin and Pancreatic Juice.** By V. HARLAY (*J. Pharm.*, 1899, [vi], 9, 468—470. Compare preceding abstract).—The green colour produced by the action of the juice of *Russula delica* on the products of the digestive action of pepsin on albumin or fibrin, is changed to a bright red by the addition of a few drops of an alkali, but is restored when acid is afterwards added. On similar treatment, the dark brown liquid resulting from the digestive action of pancreatic juice does not show a colour change.

With liquids resulting from a pancreatic digestion of albumin or fibrin, bromine water produces a precipitate which redissolves when shaken, giving rise to a red liquid, changing to a reddish-purple on further addition of bromine, a brownish-purple precipitate being finally formed. With liquids resulting from the digestive action of pepsin, only a slight turbidity and a faint, dirty violet coloration are produced, a yellowish precipitate being formed on the addition of excess of bromine.  
H. R. LE S.

**Solubility of Proteoses and Peptones in Alcohol.** By JEAN EFFRONT (*Bull. Soc. Chim.*, 1899, [iii], 21, 676—680).—The use of alcohol for the separation of the products of peptic digestion has been proposed by several experimenters, but little is definitely known regarding the actual solubility of the substances concerned. The

relative proportion of soluble and insoluble matter yielded by different specimens of commercial peptone varies greatly, according to the amounts of alcohol and peptone employed, and this result appears to be due not so much to real differences between the products examined as to their acidity. Experiment shows that the precipitate formed by adding alcohol to peptone solutions decreases rapidly as the amount of acid present increases, until finally no precipitate is obtained. It is only by working with neutral solutions that concordant results can be obtained. N. L.

**Histones.** By IVAR BANG (*Zeit. Physiol. Chem.*, 1899, 27, 463—486).—The term histone has been applied to various proteids; it was first used by Kossel for a proteid extracted from nucleated red blood corpuscles with hydrochloric acid. Next Lilienfeld separated from the thymus, spleen, and testis a histone combined with nuclein (nucleo-histone); then Mathews regarded the substance arbacin, which he prepared from the sea-urchin, *Arbacia*, as a histone, and, lastly, Schulz regards globin, the proteid constituent of hæmoglobin, as belonging to the same category. These four substances differ from each other very considerably in elementary composition, and the present inquiry was to determine whether the histones should be regarded as a separate, well characterised group of proteids. The substances examined were the four just mentioned, except that, in place of arbacin, the similar substance scombrine, prepared from mackerel sperm, was used. It is admitted that the histones give no single distinctive reaction, but from the fact that all give a certain number of reactions, the group is considered to be sufficiently well defined. These reactions are the following: (1) They are precipitated by ammonia, and the precipitate is insoluble in excess of that reagent in the presence of ammonium salts; (2) they are precipitated by nitric acid; the precipitate dissolves on heating, and reappears on cooling; (3) they are precipitated by boiling in a neutral solution, except when the solution contains little or no salt; (4) neutral solutions are precipitated by alkaloidal reagents, and (5) they precipitate albumin from its solutions. W. D. H.

**Definite Compounds of Proteids [with Mineral Acids].** By THOMAS BURR OSBORNE (*J. Amer. Chem. Soc.*, 1899, 21, 486—493).—The author finds that the proteids hitherto prepared are definite compounds of protein with mineral acids, or mixtures of such compounds. All these substances are acid to phenolphthalein, slightly acid or neutral to litmus, and alkaline to lacmoid or tropæolin; by means of the last two indicators, it is found that proteids are capable of combining with further quantities of acid.

In the case of edestin, the nature of the combined acids depends on the method of preparation; thus, when precipitated from sodium chloride solution, it contains mostly hydrochloric acid, and when thrown down from ammonium sulphate solution, it is united to sulphuric acid. When either product is suspended in water and made neutral to phenolphthalein by dilute caustic potash, the alkali unites with the acid from the edestin and the proteid is precipitated in the free state. Thus obtained, edestin is insoluble in water, but dissolves readily in decinormal acid or alkali. It is soluble also in 10 per cent. aqueous

sodium chloride; the solution is neutral to phenolphthalein, but alkaline to litmus and lacmoid, and when heated on a water-bath is slowly and imperfectly coagulated. From this brine solution, the edestin is slightly precipitated by saturating with salt, more so by saturating with magnesium sulphate, and completely on saturating with sodium sulphate at  $34^{\circ}$ . On dialysing the liquid obtained by gradually mixing a 10 per cent. sodium chloride solution of edestin with an equal volume of the same salt solution containing 1 c.c. of decinormal hydrochloric acid per gram of edestin, a crystalline deposit is obtained, of which the part insoluble in water consists of *edestin monohydrochloride*; it separates from a diluted brine solution in octahedral crystals. On treating edestin with insufficient hydrochloric acid to completely dissolve it, the part dissolved consists of a *dihydrochloride* which is soluble in water, but is reprecipitated by the addition of very small quantities of alkali salts. It dissolves in 10 per cent. sodium chloride solution, giving a liquid from which, on dialysis, it separates in octahedra; it crystallises well from a diluted brine solution, and in either aqueous or salt solutions is acid to phenolphthalein or litmus, but alkaline to lacmoid. Sodium chloride solutions of both derivatives give a flocculent precipitate when heated at  $99^{\circ}$ , and, on saturation with sodium chloride, magnesium sulphate, or sodium sulphate, behave similarly to edestin. T. H. P.

**Egg-Albumin.** By THOMAS BURR OSBORNE (*J. Amer. Chem. Soc.*, 1899, 21, 477—485).—In the preparation of crystallised albumin, the author finds that instead of adding acetic acid to the semi-saturated ammonium sulphate solution of egg-albumin, as recommended by Hopkins and Pinkus (*Abstr.*, 1898, i, 456), the addition of hydrochloric acid, equivalent in quantity to the acetic acid, gives a quicker precipitation of the substance. The products thus obtained, which are acid to litmus or phenolphthalein, but alkaline to lacmoid or tropæolin, are regarded as compounds of albumin with acids. Of the first crop of crystals deposited, 1 gram required for neutralisation to litmus 2.05 c.c. of  $N/10$  KOH, and to phenolphthalein 1.30 c.c., the difference being 0.75 c.c. The mean difference for all the crystals obtained both by means of acetic and hydrochloric acids was 0.71 c.c. If the number 15,000, as given by Sabanéeff (*Abstr.*, 1890, 1215), for the molecular weight of albumin is correct, and the acid and albumin unite in molecular proportion, then 1 gram of albumin would require 0.67 c.c. of the alkali; also, if 3 mols. of acid combine with 1 mol. of albumin, then 1 gram of albumin would require for its neutralisation 2 c.c. of  $N/10$  alkali. The acid with which the albumin is united is almost entirely, if not altogether, organic, but its nature is unknown.

The coagulation of albumin is greatly influenced by the amount of acid present; exact neutralisation to phenolphthalein prevents coagulation, which, however, readily takes place on the water-bath in the presence of 3 mols. of acid to 1 of albumin.

Pure albumin gives in aqueous solution a mean specific rotation  $[\alpha]_D - 28^{\circ} 42'$ ; in decinormal acid or alkali solution, the rotation increases slightly with the amount of alkali or acid present. Several analyses are quoted in the paper. T. H. P.

**Crystallisation of Blood-Albumin.** By S. GRUZEWSKA (*Compt. rend.*, 1899, 128, 1535—1537).—The author has succeeded in crystallising blood-albumin from the guinea-pig, cat, ox, and adder. The blood is collected in a 0.2 per cent. solution of sodium oxalate and centrifugated, the cold residue being mixed with a saturated solution of ammonium sulphate to eliminate the globulines, which are filtered off. The filtered liquor is then kept cool by a freezing mixture for a time varying with the nature of the serum (22 hours at  $-1^{\circ}$  in the case of guinea-pig's blood), and when left at the ordinary temperature crystals of albumin are obtained. The serum of the guinea-pig yields five different forms of crystals, some apparently belonging to the hexagonal system. T. H. P.

**Crystalline Forms of Albumin.** By ARTHUR WICHMANN (*Zeit. physiol. Chem.*, 1899, 27, 575—593).—The author has investigated the crystalline forms of egg-albumin, serum-albumin, and lactalbumin, and concludes that they are probably identical, or at least isomorphous; thus, on adding ammonium sulphate to an aqueous solution of a mixture of egg- and serum-albumin or of all three albumins, only one crystalline modification can be obtained. It seems probable also, from their optical behaviour, that the four different crystalline modifications of serum-albumin described by Michel and Gürber belong to the hexagonal-pyramidal class of the hexagonal system, and are all derived from the same fundamental form. The crystals of serum-albumin are as a rule larger and better defined than those of either egg-albumin or lactalbumin; all three forms, however, closely resemble one another in completely absorbing the colouring matter from dilute dye solutions, becoming coloured in the process although otherwise remaining unchanged. It is noteworthy, however, that when the coloured crystals are dried they become amorphous throughout their substance, without losing their crystalline shape, whilst the undyed crystals, under similar treatment, fall to pieces in becoming amorphous. Mineral salts such as gold chloride, silver nitrate, and cadmium borotungstate are also readily absorbed by crystalline albumin; potassium permanganate, which readily acts on aqueous albumin, forming a gelatinous substance and a brown precipitate, is apparently without action on albumin crystals, beyond tinting them yellowish-brown and rendering their material amorphous without changing their shape.

The crystalline compound of ammonium sulphate with albumin, containing about 5 per cent. of the latter, described by Harnack (*Abstr.*, 1891, 476), is shown to consist merely of crystals of ammonium sulphate containing inclusions of aqueous albumin.

When crystals of egg albumin (double refraction positive) are left in contact with the mother liquor, coagulation occurs and the mass becomes isotropic; after some time, however, crystals separate having negative double refraction which differ therefore from the original form. On warming, the amorphous variety is regenerated, but this, when left, undergoes transformation into the negatively refracting modification. The crystalline, soluble variety, which also exists in an amorphous form and appears to be monotropic, is termed *a-albumin*,



and the name  $\beta$ -albumin is given to the insoluble, amorphous form, which becomes negatively double-refracting and is enantiotropic.

W. A. D.

**Composition and Hydrolysis of the Albumin of the Carob Seed (*Ceratonia Siliqua*).** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1899, 129, 228—231).—When the albumin of the grain of *Ceratonia siliqua* is heated with dilute sulphuric acid (4 : 100) at 110°, it yields a mixture of mannose (compare Alberda van Ekenstein, *Abstr.*, 1898, i, 118) and galactose, both of which the author has isolated in a crystalline form and identified by various physical properties and chemical reactions. The quantities obtained are considerable and no other sugar seems to be formed. The nature of the insoluble portion, amounting to about 1/7 of the albumin employed, is under investigation.

C. H. B.

**Molecular Weight of Proteids.** By WILHELM VAUBEL (*J. pr. Chem.*, 1899, 60, 55—71).—A review of the methods by which the molecular weight of proteids can be determined: These comprise (1) the freezing point or boiling point of a dilute solution; (2) the analysis of proteid salts, especially metallic compounds; (3) the determination of the total percentage of sulphur, and the percentage which will act on alkaline lead solutions; (4) the estimation of the proportion of halogen, &c., in substituted proteids; (5) the estimation of the quantity of the various products of hydrolysis, especially tyrosine, aspartic acid, and arginine. A summary is given of the most reliable of the results obtained by these methods with oxyhæmoglobin, globin (from hæmoglobin), crystallised serum-albumin, conglutin, egg-albumin, and casein. The author concludes that, in the case of the albumins, the data are sufficient to give a satisfactory estimate of the molecular weight, but that further information must be obtained with regard to the albumoses and peptones.

T. M. L.

**Properties of Nucleo-Proteids.** By FILIPPO BOTTAZZI (*Real. Accad. dei Linc.*, 1899, 8, 505—513).—The nucleo-proteids examined were extracted from very fresh animal organs in such a way as to remove all enzymes, the proteid and biliary substances, and the hæmoglobin. The experiments were made in Wolff bottles so arranged that no putrefying action took place.

Towards sodium carbonate solution, nucleo-proteids show an acid behaviour, the alkalinity of the solution being gradually destroyed.

On adding to a solution of splenic or hepatic proteid sufficient oxyhæmoglobin solution to cause the liquid to show distinctly the two absorption striæ in the spectroscope and allowing to remain, it is found that, after 3 to 5 hours, all traces of the oxyhæmoglobin have disappeared; if an excess of the latter is added so that the absorption striæ unite to form a wide band, the latter gradually becomes separated into two distinct parts, which finally disappear. After this, the liquid assumes a dirty, brownish colour, but at no period of the action can the spectrum of hæmoglobin, or of methæmoglobin, be detected. Although no important differences between the actions of splenic and hepatic proteids were observed, in all these experiments the nucleo-

proteid from ox liver showed itself to be the most active. The only substance exerting a decomposing action on oxyhæmoglobin similar to that attributed to the nucleo-proteid is sodium carbonate, and this is found to have a very much slower action.

When glycogen is dissolved in solutions of hepatic proteid under conditions which do not allow of the presence of an enzyme, the glycogen disappears; the best temperature is 38—40°, and it is not necessary for the liquid to be aerated. T. H. P.

**Cellular Membrane of Gentian Root.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1899, [vi], 9, 330—331. Compare *Abstr.*, 1898, i, 607, and 1899, i, 93).—Twenty-five grams of powdered gentian root which had been previously treated with cold water, boiling alcohol, and dilute sulphuric acid, were treated with a mixture of 125 grams of sulphuric acid and 42 grams of water, and left at the ordinary temperature for 24 hours; the volume was then made up to 1000 c.c., and the filtrate, after further dilution to 5000 c.c., was boiled for 6 hours. The sulphuric acid was removed by means of chalk, the liquid evaporated, and the residue recrystallised from boiling absolute alcohol, when a crystalline sugar was obtained which gave  $[\alpha]_D + 52.51$ , and from its melting point (143—144°), and that of its osazone (205°), is identified as dextrose. H. R. LE S.

**Decomposing Action of Water on Hæmatins.** By PAUL CAZENEUVE and P. BRETEAU (*Bull. Soc. Chim.*, 1899, [iii], 21, 427—428).—After being subjected to the action of boiling water and then dried at 135°, hæmatin is insoluble in cold dilute ammonia solution. Hæmatins from the blood of oxen, horses, and sheep, after being washed with boiling water on the filter for an hour or so, all showed diminished percentages of carbon, oxygen, nitrogen, and iron. The action of the hot water is thus one of oxidation. T. H. P.

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## Organic Chemistry.

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**Italian Petroleums.** By ETTORE CECCHI-MENGARINI (*Gazzetta*, 1899, 29, i, 460—470).—Petroleums from Salsomaggiore and Ozzano in the province of Parma, and from Valleia near Piacenza, have been examined. The portion distilling between 150° and 270°, which is that used for illuminating purposes, was separated into fractions with boiling points covering a space of 10°. The density of each fraction and its solubility in a mixture of equal volumes of chloroform and 93 per cent. alcohol were measured. The densities of the different fractions show very close agreement with the corresponding values for Russian petroleum, but differ greatly from those of American petroleum; the same is the case with the curves connecting the density with the solubility in the alcohol-chloroform mixture. The author concludes that Italian petroleum consists of hydrocarbons of the naphthene series. T. H. P.

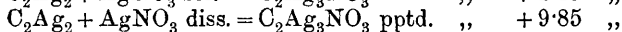
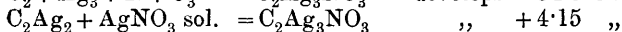
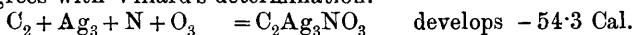
**Hydration of Acetylene.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, [vii], 17, 297—302).—An account of work already published (this vol., i, 264 and 397). G. T. M.

**Silver Derivatives of Acetylene.** By MARCELLIN P. E. BERTHELOT and MARCEL DELÉPINE (*Compt. rend.*, 1899, 129, 361—378).—The formation of disilver-acetylene by the action of acetylene on ammoniacal silver nitrate develops +15.55 Cal., and hence  $C_2 + Ag_2 = C_2Ag_2$  pptd. develops -87.15 Cal. When dried in air at the ordinary temperature, the precipitate contains 89.6 per cent. of silver, which agrees with the formula  $C_2Ag_2$ , and hence it is neither an oxide nor a hydroxide. The action of acetylene on silver oxide would develop +22.25 ( $H_2O$  gas) or +32.95 Cal. ( $H_2O$  sol.). When heated in a vacuum, disilver-acetylene detonates with a strident noise and a reddish flame, carbon being deposited on all parts of the tube. The production of flame is due to the high temperature (about 4000°) of the decomposition causing volatilisation of the carbon, the condensation of which, in its turn, develops a large quantity of heat. The compound is decomposed by gaseous hydrogen chloride and dilute hydrochloric acid, with liberation of acetylene and development of +43.25 Cal. and +8.4 Cal. respectively, but is not attacked by dilute sulphuric or nitric acid, because such reactions would be markedly endothermic. Gaseous nitric acid, however, oxidises it violently.

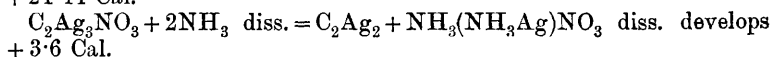
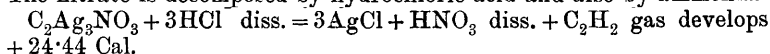
The direct formation of disilver-acetylene would absorb a much larger quantity of heat than the formation of acetylene itself. Chemical analogies indicate the possible existence of a compound  $C_2HAg$ , but thermochemical analogies indicate that it would be extremely unstable. The substitution of sodium for hydrogen in gaseous hydrides and in acetylene is always exothermic, whereas in the case of silver the reaction is endothermic with hydrogen fluoride, hydrogen cyanide, and nitric acid, and especially so with acetylene (-29.05 Cal.). Disilver-acetylene is not, however, decomposed by

water, because the action of acetylene on the silver oxide that would be found is markedly exothermic:  $C_2H_2$  gas +  $Ag_2O + xH_2O = C_2Ag_2 + (H_2O)_{x+1}$  develops + 32.95 Cal.

The action of acetylene on solutions of silver salts yields compounds of the general type  $C_2Ag_2, AgR$ , which the author regards as salts of a special radicle,  $C_2Ag_3$ , the general type then being  $C_2Ag_3R$ . The reaction  $C_2H_2$  gas +  $3AgNO_3$  diss. =  $C_2Ag_3NO_3$  pptd. +  $2HNO_3$  diss. develops + 32.4 Cal., or, if the acetylene is dissolved, + 27.1 Cal., which gives + 5.3 Cal. for the heat of dissolution of acetylene, and this agrees with Villard's determination.

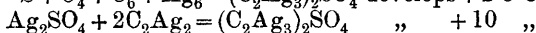
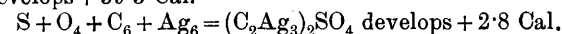
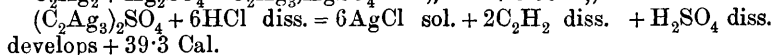
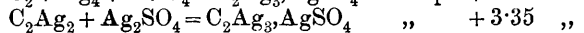
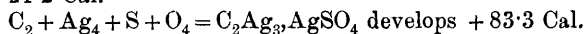
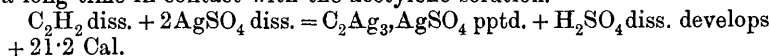


The nitrate is decomposed by hydrochloric acid and also by ammonia.



The nitrate is oxidised by strong nitric acid with liberation of nitrogen oxides and formation of some silver cyanide.

The action of acetylene on silver sulphate solution yields the compound  $C_2Ag_3, AgSO_4$  when the silver salt is in excess, and the compound  $(C_2Ag_3)_2SO_4 + C_2Ag_3, AgSO_4$  when the action of the gas is continued. The latter salt is insoluble, and hence the final compound,  $(C_2Ag_3)_2SO_4$ , described by Plimpton, is only formed when the precipitate remains for a long time in contact with the acetylene solution.



The difference between the heats of formation of the nitrate,  $C_2Ag_3NO_3$ , and the sulphate,  $(C_2Ag_3)_2SO_4$ , is practically identical with the difference between the heats of formation of silver nitrate and silver sulphate.

Silver chloride dissolved in ammonia yields three products, according to the relative proportions of silver salt and acetylene and the time of action, namely,  $C_2Ag_2Cl$ ,  $C_2Ag_3Cl$ ,  $C_2Ag_2$ , or  $C_2Ag_2(C_2Ag_3)Cl$ , and  $C_2Ag_3Cl, 2C_2Ag_2$ , the first being yellowish, the second lemon-yellow, and the third deep yellow. The decomposition of the first by hydrochloric acid develops + 11.8 Cal., and of the second + 23.3 Cal., whilst the heats of formation from the elements are - 56.4 Cal. and - 141.5 Cal. respectively. The combination of silver chloride with 1 mol. of disilver-acetylene develops + 1.75 Cal., and with 2 mols. + 3.8 Cal. It is noteworthy that the heats of formation of the compounds  $C_2Ag_3Cl$  and  $C_2Ag_3NO_3$  are practically identical, like the heats of formation of silver nitrate and chloride.

Silver iodide dissolved in potassium iodide solution containing a

small quantity of potassium hydroxide, which is renewed from time to time as the action of the acetylene is continued, yields the compound  $C_2Ag_3I, AgI$ , which is decomposed by hydrochloric acid with development of +12.65 Cal.; its heat of formation from its elements is -57.85 Cal., and from  $C_2Ag_2 + 2AgI$ , +0.90 Cal. The compound  $C_2Ag_3I$  is obtained by the carefully regulated action of potassium iodide on the corresponding nitrate; it is decomposed by hydrochloric acid with development of +13.85 Cal., and its heat of formation from its elements is -73.2 Cal. When heated, the sulphate, chloride, and iodide detonate somewhat feebly, and the nitrate violently.

The authors regard the metallic derivatives of acetylene as analogous to the nitrides derived from ammonia, and the compound  $C_2Ag_3$  as analogous to ammonium  $NH_4$ .  
C. H. B.

**Action of Acetylene on Copper.** By HANS ALEXANDER (*Ber.*, 1899, 32, 2381—2384. Compare this vol., Erdmann and Köthner, i, 21; Sabatier and Senderens, i, 555).—When pure dry acetylene is passed over spongy copper contained in a tube heated at 240—250°, the metal appears to swell enormously and finally forms a uniform, cork-like mass; when the amount of copper in the product has fallen to 2 per cent., further action ceases.

The product, when freed from liquid hydrocarbons by warmth or exposure to air, is odourless. It decomposes and becomes luminous when strongly heated in air, giving off vapours having a peaty odour. By treatment with hydrochloric acid containing ferric chloride, it loses the whole of its copper, but afterwards contains about 0.2 per cent. of iron; the substance in this case is somewhat lighter in colour, but otherwise is similar in appearance to the specimens containing copper. Analysis of the material gave an amount of carbon equal to 88—89 per cent.

The gas which passes out from the tube during the above experiment is completely absorbed by ammoniacal cuprous chloride, yielding the characteristic copper acetylide.

The formula  $C_{44}H_{64}Cu_3$  has been ascribed by Erdmann and Köthner (*loc. cit.*) to a product obtained by heating copper in acetylene at 230°, and they supposed it to be a copper-acetylene compound. The author, having repeated the experiment of these workers, concludes that the copper in their product was retained mechanically.

It is believed that the influence of the copper partakes of the nature of a contact phenomenon, and that the action consists in the polymerisation of the acetylene, and results also in the formation of naphthene-like hydrocarbons; the hydrogen liberated in the production of these substances is not set free, but would seem to be absorbed either by the resulting hydrocarbon or by the cork-like material.

A. L.

**Boiling Points of Compounds of the General Formula  $CH_3 \cdot (CH_2)_n \cdot R$ .** By ENRICO BOGGIO-LERA (*Gazzetta*, 1899, 29, i, 441—459).—The absolute boiling points of the normal compounds of homologous series of the general formula  $CH_3 \cdot (CH_2)_n \cdot R$  are equal to the square roots of numbers in arithmetical progression; this relation is expressed by the formula  $T = k \sqrt{M + c}$ , where  $T$  is the boiling point

on the absolute scale,  $M$  the molecular weight, and  $k$  and  $c$  constants whose values are in general different for different homologous series. For the value  $n = 0$  in the general formula, that is, for the first member of each series, the relation does not hold good. Tables are given showing the experimental and calculated numbers for the normal monochloro-, monobromo-, and moniodo-paraffins, amines, nitro-paraffins, ketones, alkylic formates, acetates, propionates, butyrates, valerates, hexoates, heptoates and octoates, and for alkyl-ethyl, alkyl-propyl, alkyl-butyl, alkyl-heptyl, alkyl-phenyl, alkyl-orthotolyl, alkyl-paratolyl, and alkyl-metatolyl ethers. The agreement for all these series is good, the greatest divergences being with the amines, nitro-derivatives, and ketones, where the differences between the calculated and observed temperatures are sometimes as much as 3 or 4°. For the alkylic chlorides, bromides, and iodides, the formulæ are respectively  $T = 38.66 \sqrt{M - 10}$ ,  $T = 38.98 \sqrt{M - 45}$ , and  $T = 39.1 \sqrt{M - 78}$ ; it is noticeable that the three values of  $c$ , namely,  $-10$ ,  $-45$ , and  $-78$ , stand very nearly in arithmetical progression.

T. H. P.

**Action of Nitric Acid on Saturated Hydrocarbons. VI. Nitration in Sealed Tubes and in Open Vessels. Separation of Mono- from Dinitro-compounds.** By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 1063—1064; from *J. Russ. Chem. Soc.*, 1899, 31, 57—69).—When hydrocarbons are heated with nitric acid in closed tubes, the yield of nitro-compounds obtained is dependent on the sp. gr. of the acid and the temperature at which the mixture is heated. The acid usually employed has a sp. gr. 1.075—1.2, and the temperature varies from 100—130°. Ethylbenzene and diphenylmethane, which are easily nitrated by heating in tubes at 100°, are also readily attacked in open vessels by acid of sp. gr. 1.075, and both these methods yield the same products in the case of heptane, octane, or di-isobutyl. The normal hydrocarbons form mainly secondary nitro-compounds, and the iso-hydrocarbons containing the CH<sub>3</sub>-group yield tertiary nitro-compounds; small quantities of primary nitro-compounds are also produced. Dinitro-compounds are also formed under the same conditions as mononitro-compounds, the yields being increased, however, by employing stronger acid, raising the temperature, and heating the mixture for a longer time. The dinitro-compounds may also be prepared by the action of nitric acid on the mononitro-compounds. These two classes of compounds may be separated by (1) fractionally distilling, a vacuum being used in the final distillation, (2) distilling off the mononitro-compounds in steam, or (3) by means of organic solvents. Dinitro-octane, which boils at 170—190° under 16 mm. pressure, may be separated from the mononitro-compound by the first method.

E. W. W.

**Electrolytic Reduction of Aliphatic Nitro-derivatives.** By PAUL PIERRON (*Bull. Soc. Chim.*, 1899, [iii], 21, 780—785).—The nitro-derivative is dissolved in a mixture of ethylic alcohol and dilute sulphuric acid, and submitted to electrolysis in contact with a nickel cathode, the liquid being separated from the platinum anode by a porous pot containing dilute sulphuric acid. A cathodic current

density of 0.4–0.75 ampère per square decimetre is employed. If the operation is carried out at a temperature not exceeding  $15-20^{\circ}$ , the corresponding  $\beta$ -alkylhydroxylamine is produced to the extent of 65–80 per cent. of the theoretical quantity, whilst at  $70^{\circ}$  further reduction occurs, and a scarcely inferior yield of the amine is obtained. When concentrated hydrochloric or sulphuric acid is employed, small quantities of aldehyde and hydroxylamine, besides other products, are obtained in place of the alkylhydroxylamine; the study of this reaction is being continued. Full details are given in the paper of the application of the methods described to nitromethane, nitroethane, and nitropropane. N. L.

**Action of Nitric Anhydride and Peroxide on Olefines.** By NICOLAUS I. DEMJANOFF (*Chem. Centr.*, 1899, i, 1064; from *Ann. Inst. Agron. Moscow*, 4, 155–217).—Ethylene nitrosite,  $\text{C}_2\text{H}_4\text{N}_2\text{O}_3$ , prepared by passing nitric peroxide and ethylene through ether, separates in lustrous, pseudomonoclinic needles, melts and decomposes at  $116-117^{\circ}$ , is very slightly soluble in organic solvents, insoluble in water, and when reduced with tin and hydrochloric acid forms ethylenediamine. By the action of nitric anhydride on ethylene at a low temperature, *ethylenic nitrate* is formed; it boils at  $114-116^{\circ}$  and explodes on distillation. Since the crude product, when reduced, yields acetaldehyde, ethylenediamine, and  $\beta$ -aminoethylic alcohol, it is assumed to be the compound  $\text{NO}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}_2$ . *Amylenenitrosate*,  $\text{NO}_2 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{NOH}$ , obtained by the action of nitric anhydride on trimethylethylene, melts at  $97^{\circ}$ . Analyses of the platinum salts prepared from the mother liquor indicated the presence of the compounds  $\text{OH} \cdot \text{C}_5\text{H}_{10} \cdot \text{NH}_2$  (?) and  $(\text{OH} \cdot \text{C}_5\text{H}_{10})_2\text{NH}$  (?). By the action of nitric anhydride on tetramethylethylene, the compounds  $\text{C}_6\text{H}_{12}\text{O}_4\text{N}_2$ ,  $\text{C}_6\text{H}_{12}\text{O}_5\text{N}_2$ , and  $\text{C}_6\text{H}_{12}\text{O}_6\text{N}_2$  are formed, according to the conditions of the experiment, whilst by the action of nitric peroxide only the two former compounds are obtained. The first compound separates in pseudomonoclinic crystals and sublimates at  $170-180^{\circ}$ . Since the corresponding amine,  $\text{NH}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{OH}$ , may be prepared by a trustworthy synthetical method, this compound must have the composition  $\text{NO} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{NO}_2$ . The amine forms pseudomonoclinic crystals, melts at  $10^{\circ}$ , and boils at  $160-161^{\circ}$  under 254 mm. pressure. The compound  $\text{NO}_2 \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{NO}_2$  separates in crystals which are unlike those of either of the other compounds, and melts at  $88-89^{\circ}$ . The third compound,  $\text{NO}_2 \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{NO}_2$ , is also obtained by the action of nitric anhydride on tetramethylethylenic oxide, and when reduced with zinc dust and acetic acid yields pinacone hydrate, whilst by the action of tin and hydrochloric acid pinacolone and ammonia are formed; it combines with hydrogen bromide to form tetramethylethylenic bromide,  $\text{C}_6\text{H}_{12}\text{Br}_2$ . The compound  $(\text{C}_4\text{H}_8\text{O}_3\text{N}_2)_2$ , prepared by the action of nitric anhydride on dimethylethylene, crystallises in colourless, pseudomonoclinic prisms, melts at  $133-134^{\circ}$ , and is insoluble in water. By varying the conditions of the experiment, a product may be obtained which, when reduced with tin and hydrochloric acid, yields methyl ethyl ketone and a compound,  $\text{OH} \cdot \text{CHMe} \cdot \text{COMe}$ , which distils over, whilst the residue contains

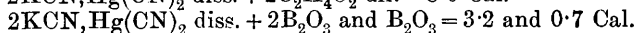
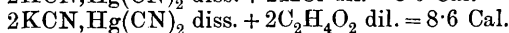
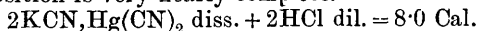
$\text{CMe} \cdot \text{N} \cdot \text{CMe}$   
 $\text{CMe} \cdot \text{N} \cdot \text{CMe}$   
 tetramethylpyrazine, a compound also formed by reducing the product of the action of nitric peroxide on dimethylethylene; it melts at 86° and boils at 189—190°. E. W. W.

**Double Cyanides.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, 17, [vii], 458—470).—Potassium silver cyanide is completely decomposed by nitric acid (1 mol. in 2 litres); the reaction ( $\text{AgCN}, \text{KCN diss.} + \text{HNO}_3 \text{ dil.} = \text{AgCN} + \text{KNO}_3 \text{ diss.} + \text{HCN diss.}$ ) develops 4.2 Cal.; an excess of the acid has no further action on silver cyanide.

Hydrochloric acid also precipitates silver cyanide from the double salt, but if the acid is in excess, the precipitate consists of a mixture of silver chloride and cyanide; this is explained by the fact that the heats of neutralisation of hydrochloric and hydrocyanic acids by silver oxide are 20.6 Cal. and 21.4 Cal. respectively. The double cyanide is more stable towards feebler acids, such as acetic, boric, arsenious, and carbonic acids, and behaves like a salt of hydrargentocyanic acid. Carbonic acid has no action on the double salt, although it reacts with potassium cyanide; in the other cases, the heat effect indicates that the decomposition is only partial. The addition of boric acid produces a slight turbidity, and the heat developed is 0.12 Cal.; a similar result is obtained with arsenious acid.

The addition of  $\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$ ,  $\text{C}_2\text{H}_4\text{O}_2$ , or  $\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2$  to a solution of  $\text{KCN}, \text{AgCN}$  develops 1.4, 2.2, or 2.6 Cal. respectively, these thermal effects being accompanied by the partial precipitation of silver cyanide and the liberation of hydrogen cyanide. The quantity of precipitate increases when the reaction is performed in open vessels. The calculated heat effect for complete decomposition is 3.8 Cal.; the values obtained from experiment all fall short of this, and it is assumed that the discrepancy is due to the formation of hydrargentocyanic acid; if this substance were quite stable, there would be no appreciable thermal effect on the addition of the acetic acid; the heat developed is due to its partial dissociation into silver cyanide and hydrogen cyanide. In an open vessel, this dissociation continues, owing to the escape of the hydrogen cyanide; this accounts for the gradual increase of the precipitate. The heat of formation of the hypothetical acid is -3.8 Cal.; its metallic salts form a well-defined series, but there is no thermochemical evidence to show that its silver salt  $\text{Ag}(\text{AgCy}_2)$  differs from ordinary silver cyanide.

Potassium mercuric cyanide is completely decomposed by hydrochloric and acetic acids into mercuric cyanide, hydrogen cyanide, and the potassium salt of the reacting acid; with boric acid, the decomposition is very nearly complete.



the calculated values for complete decomposition by boric acid being 3.8 Cal. for  $2\text{B}_2\text{O}_3$  and 0.9 Cal. for  $\text{B}_2\text{O}_3$ . These results indicate that the hypothetical hydromercuric acid is even more unstable than the corresponding silver compound; its calculated heat of formation



is - 8.2 Cal. The mercuric salt of this hypothetical acid is identical with ordinary mercuric cyanide.

Potassium zinc cyanide is completely decomposed by hydrochloric acid; the reaction  $2\text{KCN}, \text{Zn}(\text{CN})_2$  diss. (1 mol. in 4 litres) +  $4\text{HCl}$  (1 mol. in 2 litres) =  $\text{ZnCl}_2$  diss. +  $2\text{KCl}$  diss. +  $4\text{HCN}$  diss. develops 17.1 Cal. at  $12^\circ$ . The decomposition by acetic acid is almost complete; at  $12^\circ$ , the reaction is accompanied by an evolution of 11.8 Cal., the calculated value for complete decomposition being 12 Cal. The double zinc salt behaves differently towards hydrogen sulphide, and carbonic and boric acids; these substances produce no immediate precipitation; the heat developed by the addition of boric acid is 1.7 Cal., the calculated value for complete decomposition being 8.4 Cal. These results indicate the probable existence of a hydrozincocyanic acid,  $\text{H}_2\text{ZnCy}_4$ , intermediate in stability between the corresponding silver and mercuric compounds; the zinc salt of this acid is, however, identical with ordinary zinc cyanide. G. T. M.

**Flash Points of Organic Compounds.** By P. N. RAIKOW (*Chem. Zeit.*, 1899, 23, 145—147).—The flash points of numerous organic compounds lie below their melting points, for example, benzene, which melts at  $+6^\circ$ , flashes at  $-8^\circ$ . The determination of the flash point is suggested as a method for testing the purity of certain organic compounds.

The flash points of aqueous solutions of ethylic alcohol of various concentrations have been determined by the aid of the usual Abel apparatus; some of the numbers obtained are as follows:

Volume per cent. of									
ethylic alcohol ...	100	90	70	50	30	15	10	4	
Flash point ...	$12^\circ$	$16.5^\circ$	$21^\circ$	$24^\circ$	$29.5^\circ$	$41.75^\circ$	$49^\circ$	$68^\circ$	

Although the flash point rises with the dilution of the alcohol, the increment is not proportional to the dilution.

The maximum contraction in volume is obtained when 51.9 vols. of alcohol are mixed with 48.1 vols. of water, and as there is no sharp break in the flash point with an alcohol of this concentration, the author argues against the idea of the presence of a definite hydrate in such a mixture. J. J. S.

**Non-existence of Monethylic Borate [Metaborate].** By H. COPAUX (*Bull. Soc. Chim.*, 1899, [iii], 21, 776—778).—When boric anhydride is heated with alcohol at  $125^\circ$  in an autoclave for 3 hours and excess of alcohol and triethylic borate removed from the product by distillation, a syrupy liquid is obtained which, according to Schiff (*Annalen*, Suppl. 5, 153), is ethylic metaborate,  $\text{BO}(\text{OEt})$ , produced by the action of boric anhydride on the triethylic borate first formed. The results obtained by analysis agree fairly well with this supposition, but the author considers the substance to be a mixture of polymolecular compounds, since (1) it is non-volatile and begins to decompose at  $180^\circ$ , yielding triethylic borate and a viscous residue; (2) contradictory results are obtained by cryoscopic and ebullioscopic molecular weight determinations, whereas triethylic borate is distinctly shown to be unimolecular; (3) the reaction, assumed by Schiff, between boric

anhydride and triethylic borate could not be obtained; (4) when treated with zinc ethyl or boron fluoride, it yields the same products as are obtained from triethylic borate, namely, boron ethyl,  $\text{BEt}_3$ , and difluorethylic borate,  $\text{BF}_2 \cdot \text{OEt}$  respectively. N. L.

**Crotonaldehyde.** By ERNEST CHARON (*Ann. Chim. Phys.*, 1899, 17, [vii], 197—288. Compare Abstr., 1896, i, 407, 637, and 661).—The paper contains details of work already published, together with a description of certain new derivatives of crotonaldehyde.

$\beta\gamma$ -Dibromobutylic alcohol,  $\text{CHMeBr} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{OH}$ , first obtained by Lieben and Zeisel as a viscid oil, crystallises in colourless prisms melting at  $32^\circ$ ; it is readily soluble in ordinary solvents.

$\alpha$ -Chloro- $\beta$ -butylene (crotonylic chloride),  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2\text{Cl}$ , prepared by digesting crotonylic alcohol with concentrated hydrochloric acid, is a mobile, colourless liquid boiling at  $77^\circ$  under ordinary pressure, and has a sp. gr. 0.9491 at  $0^\circ$ .

$\alpha\beta\gamma$ -Trichlorobutane,  $\text{CHMeCl} \cdot \text{CHCl} \cdot \text{CH}_2\text{Cl}$ , obtained by passing chlorine into a chloroform solution of the preceding compound, is a colourless, oily liquid having an agreeable odour; it boils at  $79$ — $80^\circ$  under 32 mm. pressure, and has a sp. gr. 1.3241 at  $0^\circ$ .

$\alpha$ -Chloro- $\beta\gamma$ -dibromobutane,  $\text{CHMeBr} \cdot \text{CHBr} \cdot \text{CH}_2\text{Cl}$ , is a colourless liquid of camphor-like odour; it boils at  $93$ — $94^\circ$  under 15 mm. pressure, and has a sp. gr. 1.9478 at  $0^\circ$ .

$\alpha$ -Bromo- $\beta$ -butylene (crotonylic bromide),  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2\text{Br}$ , a liquid resembling allylic bromide, is prepared from crotonylic alcohol and concentrated hydrobromic acid; it boils at  $102$ — $103^\circ$  under ordinary pressure, and has a sp. gr. 1.3119 at  $0^\circ$ . An ethereal solution of this substance, when heated with dry potassium formate, yields  $\alpha\gamma$ -butadiene (divinyl),  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2$ .

$\beta\gamma$ -Dichloro- $\alpha$ -bromobutane,  $\text{CHMeCl} \cdot \text{CHCl} \cdot \text{CH}_2\text{Br}$ , produced by passing chlorine into  $\alpha$ -bromo- $\beta$ -butylene dissolved in chloroform, is a colourless liquid boiling at  $87$ — $88^\circ$  under 21 mm. pressure, and having a sp. gr. 1.6302 at  $0^\circ$ .

$\alpha\beta\gamma$ -Tribromobutane,  $\text{CHMeBr} \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ , boils at  $113$ — $114^\circ$  under 21 mm. pressure, and has a sp. gr. 2.2195 at  $0^\circ$ ; it is a colourless liquid of camphor-like odour, and reddens on exposure to air.

$\alpha$ -Iodo- $\beta$ -butylene (crotonylic iodide) is obtained colourless by distillation under diminished pressure; it boils at  $61$ — $62^\circ$  under 50 mm., and has a sp. gr. 1.6823 at  $0^\circ$ . This substance changes spontaneously into a dimeric polymeride,  $(\text{C}_{10}\text{H}_7\text{I})_2$ , which crystallises in silky needles, sublimes at  $100^\circ$ , and decomposes at  $180^\circ$ .

Octadiene (dicrotonyl),  $\text{C}_8\text{H}_4(\text{CH} \cdot \text{CHMe})$ , is prepared by the action of zinc dust or the copper-zinc couple on crotonylic bromide or iodide; the yield is 40 per cent., and greatly exceeds those obtained by similar reactions in the allylic series. The hydrocarbon is a colourless liquid boiling at  $117$ — $119^\circ$  under ordinary pressure; when treated with iodine, it yields the polymeride of crotonylic iodide.

Methylic crotonylic oxide,  $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OMe}$ , produced by treating crotonylic bromide with sodium methoxide, is a volatile liquid boiling at  $79^\circ$  under atmospheric pressure, and has a sp. gr. 0.8035 at  $0^\circ$ .

Ethylic crotonylic oxide, prepared in a similar manner to its lower

homologue, boils at  $99^{\circ}$  under atmospheric pressure, and has a sp. gr. 0.8206 at  $0^{\circ}$ .

*Dicrotonylic oxide*,  $(\text{CHMe}:\text{CH}:\text{CH}_2)_2\text{O}$ , obtained either by mixing sulphuric acid with crotonylic alcohol, or by the action of crotonylic chloride, bromide, or iodide on sodium crotonyloxide, is a colourless liquid having a penetrating odour; it boils at  $143\text{--}145^{\circ}$  under ordinary pressure, and has a sp. gr. 0.8895 at  $0^{\circ}$ .

*Ethylic  $\beta$ -dibromobutylic oxide*,  $\text{CHMeBr}:\text{CHBr}:\text{CH}_2:\text{OEt}$ , produced by adding bromine to ethylic crotonylic oxide, boils at  $116\text{--}117^{\circ}$  under 20 mm. pressure, and has a sp. gr. 1.700 at  $0^{\circ}$ . When this substance is treated with zinc dust, ethylic crotonylic oxide is regenerated.

*Dicrotonylic sulphide*,  $(\text{CHMe}:\text{CH}:\text{CH}_2)_2\text{S}$ , results from the action of sodium sulphide on crotonylic bromide; it is a colourless liquid having a garlic odour and burning taste; it boils at  $186\text{--}187^{\circ}$  under ordinary pressure, and at  $106\text{--}108^{\circ}$  under 50 mm.; it has a sp. gr. 0.9032 at  $0^{\circ}$ .

*Crotonylthiocarbimide*, produced by warming a methylic alcohol solution of crotonylic bromide and potassium or ammonium thiocyanate, is a colourless liquid with an odour of horseradish; it boils at  $83\text{--}85^{\circ}$  under 50 mm. pressure, and has a sp. gr. 0.9927 at  $0^{\circ}$ .

*Crotonylthiocarbamide*,  $\text{CHMe}:\text{CH}:\text{CH}_2:\text{NH}:\text{CS}:\text{NH}_2$ , prepared by heating the preceding compound with aqueous ammonia, crystallises from water in colourless scales melting at  $105^{\circ}$ ; it is readily soluble in alcohol or ether.

On mixing crotonaldehyde pinacone (dipropenylic glycol) with bromine in chloroform solutions, two *tetrabromo*-derivatives are obtained; the first crystallises in needles and melts at  $123^{\circ}$ ; the second separates in scales and melts at  $171^{\circ}$ . The acetyl derivative of the tetrabromo-compounds crystallises in colourless prisms and melts at  $141^{\circ}$ . When dipropenylic glycol is treated with hypochlorous acid, a *dichlorohydrin*,  $\text{C}_8\text{H}_{16}\text{O}_4\text{Cl}_2$ , is produced; it crystallises in colourless scales melting at  $222\text{--}223^{\circ}$ ; the *tetracetyl* derivative of the chlorohydrin melts at  $270^{\circ}$ .

G. T. M.

**Influence of Water on the Velocity of Ether Formation.**  
By CORNELIS A. LOBRY DE BRUYN and ALPHONSE STEGER (*Rec. Trav. Chim.*, 1899, 18, 311—325).—A study of the reactions  $\text{NaOEt} + \text{MeI}$  and  $\text{NaOEt} + \text{EtI}$  in ethylic alcohol shows that the velocity coefficient decreases as the dilution of the alcohol increases, whilst in the case of the reactions  $\text{NaOMe} + \text{MeI}$  and  $\text{NaOMe} + \text{EtI}$  in methylic alcohol, the addition of water at first produces an increase in the value of the coefficient, which, after attaining a maximum, diminishes continuously as the dilution is increased. Owing to the solubility of methylic iodide in water, it is possible to make experiments under all conditions of dilution, from absolute alcohol to pure water; with the ethylic iodide, it is not possible to employ a medium containing less than 40 per cent. of the alcohol. The velocity coefficient is calculated from determinations of the alkalinity of the solutions after given intervals of time, the temperature being maintained at  $25^{\circ}$ . The results are tabulated and the variations of the velocity coefficient with change of dilution are represented graphically. It is noticed that when the

dilution is considerable, the value of this coefficient for a given dilution is not constant; as the reaction proceeds, a gradual diminution becomes apparent; this may be due to the change in the concentration of the ions, the dissociation of NaOEt or NaOMe being different from that of NaI.

The velocity of the reaction  $\text{NaOEt} + \text{MeI}$  in absolute ethylic alcohol is six times as great as that of  $\text{NaOMe} + \text{MeI}$  in absolute methylic alcohol, although the reagents are far more dissociated in the latter solvent; moreover, the velocity of the reaction  $\text{NaOEt} + \text{MeI}$  in ethylic alcohol is 30 times greater than that of the reaction  $\text{NaOMe} + \text{EtI}$  in methylic alcohol. It appears, therefore, that the velocity of reactions occurring in media other than water depends, not only on electrolytic dissociation, but also on other undetermined factors.

G. T. M.

**Preparation of Formose by means of Amorphous Lead Hydroxide.** By CORNELIS A. LOBBY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1899, 18, 309—310).—Amorphous lead hydroxide is precipitated on adding caustic potash to a solution of basic lead acetate; when dried at ordinary temperatures, it forms a white powder which is more active than lead oxide in promoting the condensation of formaldehyde to formose. A dilute solution of the aldehyde is heated with a small quantity of the hydroxide for one hour at  $100^\circ$  and evaporated down to a syrupy consistence; the residue is dissolved in a mixture of methylic and ethylic alcohols and treated with ether to precipitate the lead salts of any organic acids present; the filtrate now contains formose, the yield being about 70 per cent. of the formaldehyde employed. Lead hydroxide, when precipitated by ammonia, appears to be crystalline, and has no action on formaldehyde; negative results were also obtained with sodium, potassium, zinc, copper, or cadmium hydroxides, whilst 10 per cent. of formose was obtained by the use of calcium hydroxide.

G. T. M.

**New Hexosazones from Glycerol and Formaldehyde.** By OSCAR LOEW (*Chem. Zeit.*, 1899, 23, 542—543 and 566—567).—Bromine and sodium hydroxide react with glycerol, yielding a mixture of dihydroxyacetone and glyceraldehyde (Fischer and Tafel). Sodium carbonate was employed in place of the hydroxide, the mixture allowed to remain for 12 hours at a low temperature, and the condensation was completed by warming for several days at  $55^\circ$ , until the product gave no deposit of glycerosazone on treatment with phenylhydrazine hydrochloride in acetic acid solution. The condensation product yields an *osazone*,  $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$ , melting at  $157^\circ$ ; it is readily soluble in alcohol, ether, acetone, or ethylic acetate, moderately so in benzene or chloroform; it also dissolves in about 400 times its weight of boiling water, from which it crystallises in long, felted, thread-like masses. The author terms the compound *morfosazone* on account of its resemblance to formosazone, from which, however, it differs in crystalline habit and in melting point. Morfose is formed, together with formose, when formaldehyde solution is shaken with calcium

hydroxide, filtered, and warmed on the water-bath after the addition of alcohol. At a higher temperature ( $80^{\circ}$ ) and in the presence of a smaller quantity of calcium hydroxide, a third sugar is obtained, the osazone of which melts at  $167^{\circ}$  and somewhat resembles that mentioned by Fenton (*Trans.*, 1897, **71**, 379). When the crude glycerose obtained by the action of bromine and sodium carbonate on glycerol is treated with acetic acid until all the bicarbonate is decomposed, and then with calcium hydroxide, a further condensation ensues, which is complete in 4 hours at  $20^{\circ}$  or in 5 minutes at  $82^{\circ}$ . The product yields an osazone, *lycerosazone*, which crystallises from hot water in very characteristic spindle-shaped crystals melting at  $152^{\circ}$ ; it dissolves less readily than formosazone in ether, chloroform, turpentine, or benzene. J. J. S.

**Rotatory Power of Sugar Solutions.** By E. MASCART and H. BÉNARD (*Ann. Chim. Phys.*, 1899, **17**, [vii], 125—144).—The paper contains details of experiments made, at the request of the French Ministry of Finance, with the object of determining accurately the rotatory power of a sugar solution of convenient strength for use in commercial analyses; it is not suitable for abstraction. G. T. M.

**Groups of Carbohydrates.** By VENTURO ZANOTTI (*Chem. Centr.*, 1899, **i**, 1209—1210; from *Ann. Soc. Chim. Milano*, 1899, **27**—39).—The shells of nuts contain compounds which yield xylose and dextrose, and whose constitution is very different to that of cellulose. Phenylxylosazone melts at  $153^{\circ}$ . Generally speaking, dextrin always occurs associated with xylin, and galactin with arabin in plants.

*Penicillium glaucum*, in common with other low organisms, contains a small quantity of mannin.

When cellulose prepared from purified cotton wool was oxidised by (a) hydrochloric acid and potassium chlorate, (b) chromic and sulphuric acids, (c) potassium permanganate and sulphuric acid, "oxycelluloses" of the following compositions were obtained:

	Oxycellulose.		
	a.	b.	c.
Ash .....	0.15	0.50	0.30
Carbon .....	43.66	42.96	42.52
Hydrogen .....	6.60	6.52	6.56
Oxygen .....	49.74	50.52	50.92
Furfuraldehyde .....	0.80	3.05	1.90
Cellulose .....	45.20	26.05	39.92
Oxycellulose, by difference ...	54.80	73.95	60.08

The action of alkalis showed that these substances are really mixtures of cellulose and hydrocellulose with their oxidation and decomposition products. E. W. W.

**Molecular Weight of Soluble Starch.** By H. FRIEDENTHAL (*Chem. Centr.*, 1899, **i**, 924; from *Centr. Physiol.*, **12**, 849—850).—By dissolving "ozone-starch," a commercial soluble starch, in water and precipitating with alcohol, a product was obtained the molecular

weight of which was found by Beckmann's method to be 9450. The empirical formula of the starch being  $3C_6H_{10}O_5 + H_2O$ , this result would indicate a molecular formula 20 ( $C_{18}H_{30}O_{15} + H_2O$ ), but the formula  $60 C_6H_{10}O_5 + H_2O$  corresponds still better with the number obtained.

E. W. W.

**Combination of Colloidal with Crystalloidal Substances.** By A. FRIEDENTHAL (*Chem. Centr.*, 1899, i, 1161—1162; from *Centr. Physiol.*, 13, 54—58).—The addition of 1 per cent. of iodine to a 5 per cent. solution of starch does not lower the freezing point of the solution by a measurable amount, hence iodide of starch would appear to be a chemical compound rather than a simple solution. The freezing point of a solution of iodine in potassium iodide, however, is considerably lowered by adding large quantities of soluble starch. The varying results obtained by the author and by Küster indicate that this method is not applicable in the case of starch, just as physico-chemical methods give untrustworthy results with compounds of such high molecular weight as albumin and albumoses, since the least quantity of ash causes great errors.

E. W. W.

**Cellulose and Starch.** By ZDENKO H. SKRAUP (*Ber.*, 1899, 32, 2413—2414).—Franchimont found that cellulose yields acetyl compounds when treated with a mixture of acetic anhydride and sulphuric acid, and that one of these is crystalline, and has the composition of a triglucose containing 11 acetyl groups.

It has been found that if low temperatures and small quantities of sulphuric acid are used, the products are more complicated than when these precautions are not observed.

[With HUGO HAMBURGER.]—Starch, on moderated acetylation, gives an acetyl compound which, when hydrolysed with alkalis, yields a product having all the characteristic properties of soluble starch. On energetic acetylation, however, breaking down occurs, attended by addition of acetic anhydride, and besides amorphous products, pentacetylglucose melting at  $113^\circ$  is obtained; this, however, is only produced when the product is treated with water.

[With PREGL.]—Cellulose, when energetically acetylated, yields, by addition of acetic anhydride, a substance which crystallises from ethylic acetate or alcohol in beautiful, long needles melting at  $228^\circ$ , and is identical with Franchimont's substance; determination of the molecular weight of the compound, however, shows that his view of its constitution is incorrect, and that it is either a pentacetylhexose or a heptacetylheptose. On hydrolysis with alkali, it does not yield glucose, but a substance sparingly soluble in alcohol although readily soluble in water, which gives, not an osazone, but a phenylhydrazone melting at  $194^\circ$ , and closely resembling mannosephenylhydrazone in many particulars.

By very careful acetylation, cellulose and starch yield derivatives which contain more acetyl than might be anticipated on the basis of the usual formulæ for these substances.

A. L.

**Cellulose.** By G. BUMCKE and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 2493—2507).—The so-called oxycellulose, obtained by treat-

ing cellulose with hydrogen peroxide, possesses many of the properties usually associated with aldehydes; it is strongly reducing, combines with phenylhydrazine, and restores the colour to a solution of magenta and sulphurous acid. Cellulose itself is destitute of these properties, and the fact that oxycellulose behaves like a reducing agent tells against the view that the action is one of oxidation; here, as in the case of cane sugar (Wurster, *Centr. Physiol.*, 1, 33), hydrogen peroxide acts as a hydrolytic agent. Ash-free filter paper was treated at ordinary temperatures with varying quantities of re-distilled hydrogen peroxide (4 to 60 per cent.) until the fibres were completely disintegrated. Analyses of the dried product gave numbers corresponding with  $6C_6H_{10}O_5, H_2O$ ,  $7C_6H_{10}O_5, H_2O$ , or  $8C_6H_{10}O_5, H_2O$ ; the analytical results are not conclusive, owing to the molecular complexity of the substances involved. This product the authors call *hydralcellulose*; it has no action on iodine solution, but when treated with excess of phenylhydrazine, it yields a hydrazone containing 1.69 to 1.83 per cent. of nitrogen: a phenylhydrazone having the composition  $C_{36}H_{62}O_{30} \cdot N_2HPh$  should contain 2.6 per cent. Cellulose itself is not acted on by phenylhydrazine. The hydrazone partly dissolves in caustic soda solution, but the soluble and insoluble portions alike contain the same percentage of nitrogen. When tested with Fehling solution, the reducing power of hydralcellulose is found to be 1/12th that of dextrose. On acidifying the solution of hydralcellulose in this reagent, a flocculent, white precipitate is obtained; this product, "*acid-cellulose*," is also produced by warming hydralcellulose with excess of 10 per cent. caustic soda solution; the yield is about 33 per cent., an insoluble substance having the properties of cellulose being formed at the same time; the reaction appears to be quite analogous to the action of alkalis on certain aldehydes; hydralcellulose (aldehyde) = cellulose (alcohol) + acid-cellulose (acid). Acid-cellulose may also be prepared directly from cellulose, either by heating this substance with a 30 per cent. solution of caustic soda until the whole has passed into solution, or by acidifying the solution of cellulose in Schweitzer's reagent; in the former process, the yield is 39 per cent., in the latter, the substance is accompanied by a small amount of hydralcellulose.

Acid-cellulose readily dissolves in dilute alkalis, but not in aqueous ammonia; it has an acid reaction, decolorising an alkaline solution of phenolphthalein, and does not react with Fehling's solution, phenylhydrazine, or iodine solution; when left in contact with concentrated hydrochloric acid, it undergoes hydrolytic decomposition into soluble products which have reducing properties. When dried at 105°, acid-cellulose loses water and becomes converted into *acid-celluloselactone*,  $C_{36}H_{60}O_{31}$ ; this substance forms a hard, horny mass insoluble in alkalis.

The action of concentrated nitric acid on cellulose is not simply one of nitration, hydrolytic changes are simultaneously produced so that the same products are obtained by nitrating cellulose, hydralcellulose, and acid-celluloselactone. The dried substance was in each case mixed with 10 parts of nitric acid of sp. gr. 1.48 and heated for some time at 85°; the product was soluble in acetone and was separated

into two fractions differing in solubility in ethylic alcohol. The more soluble substance forms a friable mass, whilst the other is obtained in coherent films. Both substances, derived either from cellulose, hydralcellulose, or acid-cellulose prepared by Schweitzer's reagent, have the same composition, and gave analytical numbers agreeing with the formula  $\{ \frac{2}{3}C_{72}H_{106}O_{44}(NO_3)_{18}, \frac{1}{3}C_{72}H_{112}O_{50}(NO_3)_{12} \}$ ; the more soluble nitro-derivative obtained from the acid-celluloselactone, prepared with cellulose and caustic soda solution, also had this composition, but the less soluble substance contained more of the dinitro-compound. The more soluble substance was further identified by determining its rotatory power in acetone solution and its exploding point. The molecular weight determined in acetone solution by the ebullioscopic method showed that the molecular complexity of the nitro-compound, whether obtained from cellulose, hydralcellulose or acid-celluloselactone, is the same, namely, 1350. The experimental results indicate that the formula for hydralcellulose is probably  $6C_6H_{10}O_5 \cdot H_2O$ , and if the foregoing explanation of its formation from cellulose be accepted, the latter substance should have the formula  $C_{72}H_{120}O_{60}$ . G. T. M.

**Oxycellulose.** By O. VON FABER and BERNHARD TOLLENS (*Ber.*, 1899, 32, 2589—2601).—The oxycelluloses obtained from cellulose by the action of various oxidising agents appear to consist of varying proportions of unaltered cellulose and a substance,  $C_6H_{10}O_6$  or  $C_6H_8O_6$ , containing an additional oxygen atom, for which the name *celloxin* is proposed. This compound has not been isolated, but on heating oxycellulose with lime water, it is decomposed into a mixture of isosaccharinic and dihydroxybutyric acids, whilst the cellulose remains unaltered.

Pine-wood sawdust, when heated with moderately concentrated nitric acid for 6 hours, yields a white powder having a composition corresponding with either the formula  $C_{18}H_{28}O_{16}$  or  $C_{18}H_{30}O_{16}$ ; when the action is stopped after 3 hours, the composition of the powder obtained agrees with  $C_{24}H_{38}O_{21}$  or  $C_{24}H_{40}O_{21}$ . On distilling with hydrochloric acid, these substances yield about 7 per cent. of furfuraldehyde. The product, obtained by treating cotton wool with bromine and calcium carbonate, forms a white powder which reduces Fehling's solution, develops a violet coloration with iodine and zinc chloride, restores the colour to magenta decolorised by sulphurous acid, and is insoluble in dilute alkalis or ammonia; it corresponds in composition with the formula  $C_{12}H_{20}O_{11}$  ( $C_6H_{10}O_5 + C_6H_{10}O_6$ ), and on distillation with hydrochloric acid yields about 1.6 per cent. of furfuraldehyde. The composition of the white powder, obtained by heating cotton wool with nitric acid of sp. gr. 1.3 for  $2\frac{1}{2}$  hours on the water-bath, corresponds either with  $C_{30}H_{48}O_{26}$  or  $C_{30}H_{50}O_{26}$ ; when the action is continued for 4 hours, the composition of the product agrees with either  $C_{24}H_{38}O_{21}$  or  $C_{24}H_{40}O_{21}$ . In the first case, the product appears to contain 4 mols. of cellulose to 1 mol. of celloxin, and in the second case the proportions are 3:1. The oxycelluloses, prepared by the action of nitric acid, dissolve in dilute alkalis or ammonia to form viscid solutions having reducing properties, and differ in this respect from that obtained by the aid of bromine and calcium carbonate; all these substances, when warmed with caustic



soda, give golden-yellow solutions which reduce Fehling's solution. As the proportion of celloxin becomes greater, the solubility in dilute alkalis and the reducing power increase (compare preceding abstract). All the oxycelluloses obtained by the methods described above, when boiled with milk of lime, undergo decomposition, the celloxin being converted into the calcium salts of isosaccharinic and dihydroxybutyric acids, whilst the cellulose remains undissolved. The former acid is isolated by means of its calcium salt, which, on treatment with acids, yields isosaccharin melting at  $92-94^{\circ}$ , but having a specific rotatory power of  $49.4^{\circ}$  (not  $62-63^{\circ}$ , as usually stated). Dihydroxybutyric acid, when liberated from a solution of the calcium salt by oxalic acid, has at first a specific rotatory power of  $-2.6^{\circ}$  which after 2 days becomes  $+13.7^{\circ}$ . In preparing oxycelluloses by the action of nitric acid on cotton wool, saccharic acid and other acids containing 4 or 5 atoms of oxygen are produced as bye-products.

G. T. M.

**Action of Methylic Chloride, Bromide, and Iodide on Ammonia.** By B. DUBOWSKY (*Chem. Centr.*, 1899, i, 1066; from *J. Russ. Chem. Soc.*, 1899, 31, 34-37. Compare Menschutkin, *Abstr.*, 1895, ii, 385).—The action of a 35 per cent. solution of ammonia in methylic alcohol on methylic chloride, methylic bromide, or methylic iodide dissolved in 3-4 volumes of toluene is complete in 4 months at the ordinary temperature and products are formed which contain an amount of halogen corresponding with methylamine hydrochloride, hydrobromide, and hydriodide respectively. The same reaction takes place in 2-3 minutes at  $100^{\circ}$ . The amines obtained from these products, however, when treated with methylic bromide, yield compounds containing less bromine than that required for dimethylamine hydrobromide, &c., and from the products of the original reaction, ammonium chloride, bromide, or iodide respectively may be separated by fractionally crystallising from alcohol; the amounts of tetramethylammonium compounds are estimated by titrating the alcoholic solutions with alcoholic sodium hydroxide solution. The hydrochloride was found to contain 75.2 per cent. of ammonium and amine salts and 24.8 of tetramethylammonium chloride, the hydrobromide of 75.7 of ammonium and amine salts and 24.3 of tetramethylammonium bromide, and the hydriodide of 75.6 of ammonium and amine salts and 24.4 of ammonium iodide.

E. W. W.

**A New Amylamine.** By D. TRASCIATTI (*Gazzetta*, 1899, 29, ii, 92-101).—On reducing isonitrosodimethylethylcarbinylic cyanide,  $\text{CN}\cdot\text{CMe}_2\cdot\text{CMe}\cdot\text{NOH}$  (Guthrie's salt), in alcoholic solution by means of sodium, an amylamine,  $\alpha\beta$ -dimethylpropylamine,  $\text{CHMe}_2\cdot\text{CHMe}\cdot\text{NH}_2$ , is obtained as a colourless liquid which boils at  $84-87^{\circ}$  and has a disgusting smell. Its hydrochloride,  $\text{C}_5\text{H}_{13}\text{N}\cdot\text{HCl}$ , crystallises from alcohol in slender, silky, deliquescent needles. It forms two oxalates, the first, which has the composition  $\text{C}_5\text{H}_{13}\text{N}\cdot\text{H}_2\text{C}_2\text{O}_4$ , crystallises from alcohol in sparkling, white needles; the other,  $(\text{C}_5\text{H}_{13}\text{N})_2\cdot\text{H}_2\text{C}_2\text{O}_4$ , forms a white, crystalline mass which dissolves readily in water and decomposes without melting at  $220^{\circ}$ .

The action of nitrous acid on the amylamine gives rise to methylisopropylcarbinol. T. H. P.

**Constitution of Inorganic Compounds. XVIII. Compounds of Ethylenediamine and Propylenediamine with Salt of Bivalent Metals.** By ALFRED WERNER, W. MEGERLE, J. PASTOR, and W. SPRUCK (*Zeit. anorg. Chem.*, 1899, **21**, 201—242).—*Triethylenediaminenickel salts*.—The *sulphate*,  $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{SO}_4$ , obtained by adding ethylenediamine (3 mols.) to a concentrated solution of nickel sulphate (1 mol.), crystallises from boiling water in beautiful needles and is insoluble in alcohol. A determination of the molecular weight by the cryoscopic method gave 159.8, the theoretical number being 167.4; the molecular electric conductivity for  $v=1000$  is 224.4, which agrees with the molecular conductivity of chloropentamine cobalt sulphate, and shows that triethylenediaminenickel sulphate is soluble in water without decomposition. The *nitrate* crystallises in dark violet tablets, is somewhat easily soluble in water, and, according to the cryoscopic determinations, is then dissociated into the three ions,  $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3$  and  $2\text{NO}_3$ . The *chloride* crystallises in small, violet dihydrated prisms, the *bromide* in violet dihydrated, efflorescent leaflets, and the *iodide* in insoluble, monohydrated, reddish-violet prisms and plates. *Triethylenediaminenickel platinochloride*,  $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3]\text{PtCl}_6$ , is an amorphous, brownish-yellow precipitate and is insoluble in water.

*Tripropylenediaminenickel salts* differ from the triethylenediamine salts in that they are extremely soluble in water. The *sulphate*,  $[\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{SO}_4$ , is obtained by heating powdered nickel sulphate with the theoretical quantity of propylenediamine until a dark violet salt is obtained. It is a peach-coloured, microcrystalline powder, and gives precipitates with alkali chlorides, bromides, iodides, cyanides, or thiocyanates. The *chloride* crystallises in dihydrated, beautiful, reddish-violet leaflets, the *bromide* in dihydrated bright reddish-violet needles, the *iodide* in dihydrated reddish-violet needles, the *thiocyanate* in sparingly soluble, reddish-violet needles, and the *cyanide* in sparingly soluble, bright rose needles.

*Triethylenediaminecopper salts* are less stable than the other salts of the hexamine series, and the third ethylenediamine molecule is eliminated when they are dissolved in water; they can, however, be recrystallised from very concentrated solutions with only partial decomposition. The *sulphate*, crystallises in beautiful, blue needles and is slightly hygroscopic; the *nitrate* forms dihydrated, bluish-violet leaflets, and is not so readily decomposed by water as the sulphate.

*Triethylenediaminezinc salts*.—The *sulphate* crystallises in easily soluble, short, white needles, the *nitrate* in very hygroscopic, thick, colourless needles, the *chloride* in needles, the *bromide* in large, thick plates, and the *iodide* in pale yellow forms.

*Triethylenediaminecadmium salts*.—The *sulphate* crystallises in moderately soluble aggregates of lustrous prisms, and the *nitrate* in very hygroscopic, white crystals. The *chloride* crystallises in easily soluble white needles, the *bromide* in tablets, and the *iodide* in sparingly soluble, thick, prismatic needles.

*Triethylenediaminecobalt sulphate*, obtained as a yellowish, flesh-

coloured magma on adding ethylenediamine to a solution of cobalt sulphate, cannot be recrystallised on account of the ease with which it is oxidised, and is sparingly soluble in water.

*Tetrammine salts. Diethylenediaminenickel salts.*—The *bromide*,  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_2)_2]\text{Br}_2 + 2\text{H}_2\text{O}$ , is obtained by adding diethylenediamine (2 mols.) to a solution of nickel bromide; it crystallises in blue leaflets, is easily soluble in water, effloresces on exposure to the air, and when treated with potassium cyanide is converted into triethylenediaminenickel bromide. The *iodide* crystallises in aggregates of greyish-blue leaflets, and is easily soluble in water. The *thiocyanate*, obtained by treating the bromide with potassium thiocyanate, occurs in two isomeric forms, the one separates at once as a violet-red precipitate, the other crystallises from the mother liquor in deep, bluish-violet, six-sided plates. Both compounds can be readily recrystallised from water.

*Dipropylenediaminenickel salts.*—When propylenediamine (2 mols.) is added to a concentrated solution of nickel sulphate, a deep blue solution is obtained, from which the following salts can be prepared. The *bromide*, with  $2\text{H}_2\text{O}$ , is obtained, together with a bright blue salt, by evaporating the above solution with potassium bromide almost to dryness and then extracting the blue salt mechanically; it crystallises in reddish-blue nodules, and becomes green when dried in a desiccator. The *thiocyanate* is a violet-red salt, sparingly soluble in cold, easily so in hot water, and soluble in alcohol or ether.

*Diethylenediaminecopper salts.*—The *sulphate* obtained by precipitating a dilute solution of triethylenediaminecopper sulphate with alcohol, is a violet, microcrystalline salt, and is very easily soluble in water. The *chloride* crystallises in large, reddish-blue leaflets, and is easily soluble in water.

*Dipropylenediamineplatinous chloride*, obtained by adding propylenediamine to a solution of potassium platinosochloride and boiling the mixture in a reflux apparatus until the yellow precipitate is almost completely dissolved, crystallises in greyish-white leaflets containing water. A solution of the *base* is obtained by shaking it with freshly precipitated silver oxide; it has a strongly alkaline reaction, absorbs carbonic anhydride from the air, and has all the properties of a caustic alkali. The *bromide* crystallises in snow-white leaflets containing water, is easily soluble in water, and gradually becomes indigo-blue. The same indigo-blue salt is obtained by adding bromine to a solution of the bromide; it is a new member of the characteristic additive products of platinos- and platini-salts, and yields a colourless solution in water. The *iodide* separates in small, indefinite crystals, and is extremely soluble.

*Dichlorodipropylenediamineplatonic chloride*,  $[\text{PtCl}_2(\text{C}_3\text{H}_7\text{N}_2)_2]\text{Cl}_2$ , is obtained by the action of chlorine on an aqueous solution of dipropylenediamineplatinous chloride, and crystallises in yellowish prisms.

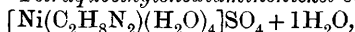
*Dibromodipropylenediamineplatonic chloride*, obtained in a similar manner to the preceding salt, separates in yellow crystals and is easily soluble in water.

*Propylenediamineplatinous chloride*,  
 $[\text{Pt}(\text{NH}_3)_2(\text{C}_3\text{H}_7\text{N}_2)_2]\text{Cl}_2$ ,  
 is obtained by cautiously adding ammonia to propylenediaminedichloro-

platinum (see later), suspended in boiling water, until a clear solution is obtained, and, after boiling off the excess of water, adding potassium platinosochloride. It is an insoluble, lilac, microcrystalline salt.

*Dibromopropylenediaminediammineplatinic chloride*, obtained by treating the preceding compound with bromine, is precipitated from the solution by alcohol and ether, or by acetone, and separates from water, in which it is extremely soluble, in beautiful, yellow crystals.

*Diammine salts.*—*Tetraquoethylenediaminenickel sulphate*,



obtained by adding ethylenediamine to a solution of nickel sulphate until triethylenediaminenickel sulphate begins to separate and then concentrating the blue solution in a vacuum, crystallises in pure blue tablets, or rosettes of needles, and is sparingly soluble in cold, easily so in hot water.

*Propylenediaminenickel thiocyanate*,  $[\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)](\text{SCN})_2 + \text{H}_2\text{O}$ , obtained from the mother liquor in the preparation of the dipropylenediamine salt, or by adding potassium thiocyanate to a solution of nickel sulphate and propylenediamine, in molecular proportion, is a greyish-blue, crystalline powder easily soluble in water.

*Dichloropropylenediamineplatinum*,  $[\text{Pt}(\text{C}_3\text{H}_{10}\text{N}_2)]\text{Cl}_2$ , obtained as a dirty yellow precipitate by adding propylenediamine to a solution of potassium platinosochloride, crystallises from hot water in beautiful, bright yellow needles.

*Tetrachloropropylenediamineplatinum*,  $[\text{Pt}(\text{C}_3\text{H}_{10}\text{N}_2)]\text{Cl}_4$ , obtained by treating the preceding compound with chlorine, separates in beautiful, lemon-yellow, flat crystals, and is easily soluble in water. When treated with propylenediamine, it yields a white, and a bright yellow, salt, which can be separated by fractional crystallisation, and are probably isomeric dichlorodipropylenediamineplatinic chlorides.

E. C. R.

**Preparation of Hydrazides and their Transformation Products.** By GUIDO PELLIZZARI (*Real. Accad. dei Lincei*, 1899, 8, 327—332).—Dibenzohydrazide can be obtained in almost theoretical yield by the action of benzoic chloride on a potassium hydroxide solution of hydrazine sulphate; crystallised from alcohol, it forms white plates melting at  $238^\circ$  (Curtius and Struve gave the melting point  $233^\circ$ ). When heated at about  $280^\circ$  for 6 hours, it is converted mainly into diphenyldiazoxole, a small quantity of 3:5-diphenyltriazole being also formed.

*Diacetohydrazide*,  $\text{N}_2\text{H}_2\text{Ac}_2$ , prepared by the action of acetic anhydride on monacetohydrazide or on a mixture of hydrazine sulphate and dry sodium acetate, crystallises from alcohol in slender needles melting at  $140^\circ$ . From aqueous alcohol, it separates, with  $1\text{H}_2\text{O}$ , in the form of colourless plates melting between  $80^\circ$  and  $100^\circ$ .

Diformohydrazide is obtained on heating hydrazine sulphate with dry sodium formate.

When heated, monacetohydrazide loses water, giving *dimethyltetrazoline*, which crystallises in prisms, melts at  $196^\circ$ , and, on boiling with acetic anhydride, yields the monaceto- and with difficulty the diaceto-hydrazide. Diacetohydrazide, when heated, gives rise to

*monacetodimethyltetrazoline*, which forms prismatic crystals and melts at 163°. Diformohydrazide gives a non-crystallisable product, which, with hydrochloric acid, evolves formic acid and yields *tetrazoline* [*dihydrotetrazine*]-hydrochloride,  $\text{NH} \begin{smallmatrix} \text{CH:N} \\ \text{N:CH} \end{smallmatrix} \text{NH} \cdot \text{HCl}$ , crystallising in transparent laminae and melting at 150°. T. H. P.

**Chloranhydride of Allylphosphorous Acid.** By M. PODLADT-SCHIKOFF (*Chem. Centr.*, 1899, i, 1067; from *J. Russ. Chem. Soc.*, 1899, 31, 30—33).—By the action of phosphorus pentachloride on allylic alcohol, *allylphosphorous chloride*,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{PCl}_2$ , and about 9 per cent. of allylic chloride are formed. The former boils at 140–5° under 742.5 mm. pressure, has a sp. gr. 1.29003 at 0°/0° and 1.2685 at 18°/0°. By the action of bromine, it yields allylic bromide, phosphoryl bromochloride, and by the action of chlorine, allylic chloride and phosphorus oxychloride. When a mixture of allylphosphorous chloride and iodine is placed in a sealed tube and exposed to the light, decomposition takes place, carbon and hydrogen iodide being formed; the same action takes place in the dark at 100°. E. W. W.

**Thioacetaldehydes.** By HEINRICH KLINGER (*Ber.*, 1899, 32, 2194—2195).—Autenrieth and Wolff (this vol., i, 580) are in error in ascribing the elucidation of the cyclic structure of trithioaldehydes to Baumann; the latter has expressly attributed it to the author (*Abstr.*, 1891, 1009).

The isomerism of the thioaldehydes is of a kind in which the isomerides have the same molecular weight and chemical structure, but different amounts of energy. For such isomerism, the author would prefer the name *dynamical isomerism*, were that not already appropriated; as it is, he proposes the term *alloergatia*. Malic and fumaric acids form the classical example of this kind of isomerism.

Liquid thioacetaldehyde, which is formed when hydrogen sulphide is continuously passed into aqueous aldehyde, has the composition  $8 \text{CH}_3\cdot\text{CHS}\cdot\text{H}_2\text{S}$ . With alkalis, it reacts like a hydrosulphide; by strong sulphuric acid and other reagents, it is converted into  $\alpha$ - or  $\beta$ -trithioacetaldehyde; when distilled, it yields ethylic bisulphide along with hydrogen sulphide and volatile sulphides and hydrosulphides, whilst a carbonaceous residue remains in the flask. C. F. B.

**Acetone Oils.** By R. DUCHEMIN (*Bull. Soc. Chim.*, 1899, [iii], 21, 798—800. Compare this vol., i, 475, 476).—The composition of acetone oil varies considerably, as is shown by the results obtained from seven different samples. The differences observed are due partly to variations in the composition of the calcium pyrolignate, which forms the original source of the oil, and partly to the more or less complete washing to which it has been subjected. Far from being always rich in methyl propyl ketone and methyl isopropyl ketone, some specimens of the oil contain only traces of these substances, and, on the other hand, as much as 50 per cent. of ketones, more especially methyl ethyl ketone, distilling below 90°. N. L.

**Dibromopinacolin.** By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1899, 23, 311).—The compound previously (*J. pr. Chem.*, 1896, [ii], 54, 429)

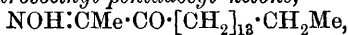
obtained by the action of concentrated hydrobromic acid on pinacone, and stated to melt at  $72^{\circ}$ , proves to be *dibromopinacolin*, probably having the constitution  $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Br}$ . It crystallises from light petroleum in large, colourless prisms melting at  $73.5\text{--}74^{\circ}$  and has a slightly irritating odour. The same product may be obtained by the action of bromine on pinacolin (compare Scholl and Weil, *Chem. Zeit.*, 1899, 23, 189). J. J. S.

**Methyl Nonyl Ketone.** By HENRI CARETTE (*J. Pharm.*, 1899, [vi], 10, 255—257).—The ketone was obtained from commercial essence of rue. Its compound with ammonium hydrogen sulphite forms nacreous crystals which are insoluble in water but very soluble in alcohol, and when heated with water yield the pure ketone. *Methyl nonyl ketone* boils at  $226^{\circ}$  ( $230.65^{\circ}$  corr.) under 766 mm., and at  $121\text{--}122^{\circ}$  ( $122\text{--}123^{\circ}$  corr.) under 24 mm. pressure, the *oxime* forms elongated prisms, sometimes 6 cm. long, which melt at  $46^{\circ}$  and are insoluble in water but very soluble in alcohol, ether, benzene, chloroform, or toluene. H. R. LE S.

**Molecular Aggregation of Dihydroxyacetone.** By GABRIEL BERTRAND (*Compt. rend.*, 1899, 129, 341—344).—Dihydroxyacetone, obtained by the action of the sorbose bacterium on glycerol (Abstr., 1898, i, 556), crystallises from its aqueous solution in a vacuum in small prisms which remain unchanged in closed vessels, but liquefy after some time if exposed to the air. The crystals are insoluble in cold absolute alcohol, ether, or acetone, but dissolve in any proportion in the boiling liquids and do not separate when the solution is cooled. The crystals melt slowly at about  $70^{\circ}$  and remain in superfusion for a considerable time; the superfused, and therefore amorphous, mass, dissolves immediately in cold absolute alcohol, acetone, or ether.

Cryoscopic determinations show that when the crystals are dissolved in water at  $5^{\circ}$  the molecular weight of the substance gradually changes from about 162 to 91. If, however, the superfused substance is dissolved, its molecular weight in solution is but little higher than 90. The molecular weight of the dissolved substance is higher the lower the temperature. If the solution is heated to  $100^{\circ}$  and then rapidly cooled, the molecular weight is 88—89, but gradually increases to 91—93 if it is allowed to remain at the ordinary temperature. These facts indicate that in crystallised dihydroxyacetone two molecules of the simple substance are aggregated together and that these are more or less completely separated when it is dissolved or fused. C. H. B.

**Transformation of Ketones into  $\alpha$ -Diketones. IV.** By GIACOMO PONZIO and AUSONIO DE GASPARI (*Gazzetta*, 1899, 29, i, 471—476).—*Isonitrosoethyl pentadecyl ketone*,



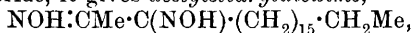
prepared by the action of isoamylic nitrite on an ethereal solution of ethyl pentadecyl ketone in presence of hydrochloric acid, crystallises from light petroleum in very slender needles melting at  $79\text{--}80^{\circ}$ , and dissolves in the cold in alcohol, ether, or benzene, but is insoluble in water; it dissolves in hot sodium or potassium hydroxide solution,

giving a yellow liquid from which it separates out unchanged on cooling. When treated with hydroxylamine hydrochloride, in molecular proportion, in presence of sodium hydroxide, it is converted into *acetyl palmityldioxime*,  $\text{NOH} \cdot \text{CMe} \cdot \text{C}(\text{NOH}) \cdot [\text{CH}_2]_{13} \cdot \text{CH}_2\text{Me}$ , which crystallises from alcohol in slender needles melting at  $147-148^\circ$  and dissolves in cold ether or hot benzene, but is almost insoluble in light petroleum.

The action of nitric acid on ethyl pentadecyl ketone gives rise to dinitroethane, palmitic acid, and isonitrosoethyl pentadecyl ketone.

*Ethyl heptadecyl ketoxime*,  $\text{CH}_2\text{Me} \cdot \text{C}(\text{NOH}) \cdot [\text{CH}_2]_{15} \cdot \text{CH}_2\text{Me}$ , crystallises from alcohol in needles melting at  $55.5-56.5^\circ$ , and is fairly soluble in ether or acetone, but only slightly so in cold alcohol or light petroleum.

*Isonitrosoethyl heptadecyl ketone*,  $\text{NOH} \cdot \text{CMe} \cdot \text{CO} \cdot [\text{CH}_2]_{15} \cdot \text{CH}_2\text{Me}$ , crystallises from light petroleum in silky needles melting at  $80-81^\circ$ , and is fairly soluble in cold alcohol, benzene, or ether. With hydroxylamine hydrochloride, it gives *acetyl stearyldioxime*,



which separates from alcohol in slender needles melting at  $120-121^\circ$ , and is soluble in the ordinary organic solvents except cold light petroleum, in which it is almost insoluble. With nitric acid, ethyl heptadecyl ketone yields dinitroethane, stearic acid, and isonitrosoethyl heptadecyl ketone.

T. H. P.

**Relative Strengths of Acids.** By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1899, 18, 298—301).—Congo red papers, prepared by soaking blotting paper in a dilute alcoholic solution of the dye, are used in demonstrating qualitatively the relative strengths of acids, the concentration of the acid solutions employed varying from  $N/10$  to  $N$ . The colour changes to various shades of violet and blue, the strongest acids producing the bluest shades. In this way, differences may be observed between acetic and formic, glycollic, lactic, and propionic acids; also between succinic and maleic and dibromosuccinic acids. The increase in strength resulting from the successive addition of chlorine may be shown in the case of acetic acid and its chloro-derivatives; the increase due to the substitution of hydrogen by hydroxyl is indicated by succinic, malic, and tartaric acids, whilst a gradual decrease of acidity is observed with the following series: oxalic, malonic, and succinic acids.

G. T. M.

**Chlorostearic Acid.** By ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1070; from *J. Russ. Chem. Soc.*, 1899, 31, 100—103).—Chlorostearic acid could not be prepared by Piotrowski's method of passing hydrogen chloride into a solution of oleic or elaidic acid and allowing the product to remain at the ordinary temperature (Abstr., 1890, 1396), but it was obtained when the mixture was heated at  $150^\circ$  for seven hours. Chlorostearic acid crystallises from ether in small nodules, and melts at  $38-41^\circ$ ; on cooling, the molten mass undergoes conversion into a modification which melts at  $20-22^\circ$ , and gradually changes into the original acid. By the action of potassium hydroxide on the chlorostearic acid obtained either from oleic or elaidic acid, the same hydroxystearic acid is formed.

E. W. W.

**Action of Acetic Anhydride on Fatty Acids.** By ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1070; from *J. Russ. Chem. Soc.*, 1899, 31, 103—106).—When palmitic acid is heated with an equal weight of acetic anhydride at 150° for six hours, palmitic anhydride melting at 55—56° is obtained. Stearic anhydride, prepared from stearic acid in a similar manner, melts at 71—77°. Oleic acid yields only an impure *oleic anhydride* which melts at 22—24°, and erucic acid an *anhydride* melting at 47—50°. This reaction may be used generally for the preparation of the anhydrides of the higher fatty acids, hence in Benedikt and Ulzer's method of determining the hydroxyl groups in hydroxy-acids (*Ber. Akad. Wiss. Wien*, 95, [ii], 110), after hydrolysing the acetyl compound, it is necessary to distil off the acetic acid.  
E. W. W.

**Oleic Acid.** By WILHELM FAHRION (*Chem. Zeit.*, 1899, 23, 770).—A specimen of pure oleic acid, which had been kept in a glass bottle for some three years, contained a substance insoluble in alkali. This is best extracted by shaking the neutral aqueous alcoholic solution with light petroleum. The amount of this neutral substance was about 5.53—5.67 per cent., its iodine number 53.3—54.8; it appeared, however, to be a mixture of a crystalline substance and an oil, the latter having the same percentage composition as oleic acid.  
J. J. S.

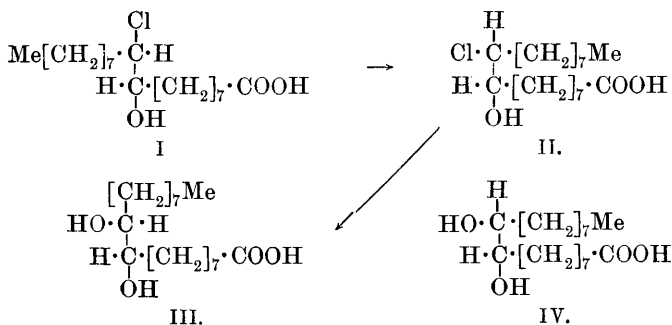
**Isomerism of Oleic and Elaidic Acids, and of Erucic and Brassidic Acids.** By ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1068—1070; from *J. Russ. Chem. Soc.*, 1899, 31, 76—100).—Chlorohydroxystearic acids were prepared from oleic, iso-oleic, and elaidic acids, and chlorohydroxybehenic acids from erucic, iso-erucic, and brassidic acids by means of the additive compounds formed with hypochlorous acid. In most cases, it was impossible to obtain a pure product, and the partially purified compound was used in the following reactions. By the action of aqueous or alcoholic potash on the chlorohydroxystearic acid prepared from elaidic acid, the dihydroxystearic acid melting at 136.5° is formed. This acid is also obtained by oxidising oleic acid with potassium permanganate (A. Saytzeff), whilst elaidic acid, on oxidation by permanganate, yields the dihydroxystearic acid melting at 99—100°. The latter acid is also formed by the action of potassium hydroxide on the chlorohydroxystearic acid obtained from oleic acid.

Similar isomerides are prepared by the action of potassium hydroxide solution on erucic and brassidic acids.

When the chlorohydroxybehenic acid, obtained from erucic acid, is treated with aqueous or alcoholic potash, the dihydroxybehenic acid is formed which melts at 99—100°; the latter acid is also a product of the oxidation of brassidic acid with potassium permanganate. The chlorohydroxybehenic acid from brassidic acid yields the dihydroxybehenic acid melting at 133°; and this acid is also prepared by the oxidation of erucic acid. By the action of potassium hydroxide on the additive compounds of hypochlorous acid with iso-oleic and iso-erucic acids, a dihydroxystearic acid corresponding with oleic acid is formed,



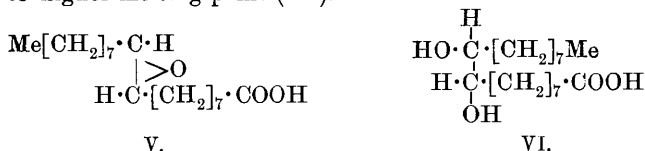
The formation of the dihydroxystearic acid of the lower melting point from oleic acid is represented as follows (I—III):—



The dihydroxystearic acid of higher melting point (IV) is formed from elaidic acid in a similar way. The intramolecular change from (I) to (II) may either occur during the addition of hypochlorous acid, or during the action of the potassium hydroxide, but it cannot take place at a later stage, for the dihydroxystearic acid melting at 93—95°, prepared by oxidising elaidic acid, undergoes no change when treated with potassium hydroxide.

When oleic and erucic acids are heated with sulphurous anhydride or sodium hydrogen sulphite, 50 per cent. of the acids are converted into elaidic and brassidic acids respectively (*J. Russ. Chem. Soc.*, 24, 477), and elaidic acid, when similarly treated, yields oleic acid, only 20 per cent of the acid, however, being attacked. In these reactions, sulpho-acids are probably intermediate products.

By the action of silver oxide on the chloro-, or, better, on the bromo-hydroxystearic acid prepared from oleic and elaidic acids, the dihydroxystearic acid of higher melting point is formed together with another compound not yet examined. The abnormal formation of this dihydroxy-acid is probably due to the high temperature of the reaction. When the chlorohydroxystearic acid obtained from oleic acid is converted into the monacetyl derivative of the dihydroxy-acid, and this then hydrolysed, the dihydroxystearic acid melting at 128—129° is formed, whilst from elaidic acid, under similar conditions, two dihydroxystearic acids are obtained, the one melting at 127—128° and the other at 93—95°. By the action of barium hydroxide on the chlorohydroxystearic acid prepared from elaidic acid, a glycidic acid (V) is formed which melts at 57—60°, and, when treated with potassium hydroxide or dilute sulphuric acid, yields the dihydroxystearic acid of higher melting point (VI).



The chlorohydroxystearic acid prepared from oleic acid, when treated

with barium hydroxide, yields glycidic acid in an uncrystallisable form, and this acid, when hydrolysed, forms the dihydroxystearic acid of lower melting point, whilst the chlorohydroxy-acid from iso-oleic acid forms the glycidic acid melting at 57—60°, and the dihydroxystearic acid of higher melting point. The chlorohydroxy-acid from elaidic acid is thus less stable than that from oleic acid, for it is changed into its stereoisomeride even by the action of weak reagents, whilst the action of sulphurous anhydride on elaidic and oleic acids shows that of these acids the former is the more stable. E. W. W.

**Elaidic Anhydride.** By M. EMELJANOFF and ALEXIUS ALBITZKY (*Chem. Centr.*, 1899, i, 1070; from *J. Russ. Chem. Soc.*, 1899, 31, 106—107).—Elaidic anhydride, prepared by the method described in a preceding abstract (p. 862), melts at 49—51·5°. By passing ammonia into the ethereal solution of the anhydride, the *amide*, which melts at 93—94°, is formed. E. W. W.

**Wood Oil.** By MORIZ KITT (*Chem. Zeit.*, 1899, 23, 23, 38).—This oil, which occurs to the extent of about 40 per cent. in the seeds of *Aleurites cordata* (belonging to the *Euphorbiaceæ*, and chiefly found in Japan), has been often the subject of investigation (compare Abstr., 1898, i, 628). The author's results are as follows: An oil, labelled "Yutshing," of a pale yellow colour, has a sp. gr. 0·9413 at 15°; saponification number, 190·7—191·0; iodine number, 157·5—158·4; acidity, as oleic acid, 3·90; melting point of the fatty acids, 35—39·5°; saponification number of the acids, 197·3—197·8; and yield of insoluble fatty acids about 82 per cent. Another oil, much darker in colour, and of greater viscosity, was also investigated; the tabulated results do not greatly differ from the foregoing, the difference being most marked in the acidity number (6·95). This oil was reinvestigated after it had been solidified by exposure to light, and the results were practically the same. Wood oil has the remarkable property of gelatinising when heated to 282°; it then is only partially soluble in benzene. The results obtained from this product, including the acetyl number, are given in tables. L. DE K.

**The Fatty Oil of Tropæolum Majus.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 471—474).—The oil extracted by ether from the pulverised seeds of *Tropæolum majus* consists largely of trierucin,  $C_3H_5(C_{22}H_{41}O_2)_3$ . When this glyceride is mixed with dilute nitric acid and is then treated with potassium nitrate, it is converted into tribrassinin, which melts at about 54° (not 47°).

When the oil is hydrolysed with caustic soda, phytosterol, equal in amount to 0·91 per cent. of the oil, resists hydrolysis. From the alkaline solution, erucic acid can be isolated; nitric acid and potassium nitrite convert it into brassidic acid much more readily than they convert trierucin into tribrassinin. C. F. B.

**Vinylglycollic ( $\alpha$ -Hydroxybutenoic) Acid.** By G. VAN DER SLEEN (*Rec. Trav. Chim.*, 1899, 18, 302—304).—A preliminary communication dealing with vinylglycollic acid,  $CH_2\cdot CH\cdot CH(OH)\cdot COOH$ . When treated with caustic soda, this substance yields three crystalline

acids, one of which is probably identical with the propionylformic ( $\alpha$ -ketobutenoic) acid,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$ , obtained as an oil by Claisen and Moritz (*Trans.*, 1880, 37, 691); the other products are being investigated. G. T. M.

**Constitution of Inorganic Compounds. XIX. Oxalato-platinum Compounds.** By ALFRED WERNER and E. GREBE (*Zeit. anorg. Chem.*, 1899, 21, 377—388).—Sodium platino-oxalate,  $\text{Na}_2\text{Pt}(\text{C}_2\text{O}_4)_2 + 4\text{H}_2\text{O}$ , prepared by adding sodium hydroxide to the copper coloured sodium salt formed by the action of oxalic acid on sodium platinate until a yellow solution is obtained, crystallises in long, lemon-yellow prisms, and yields a bright red, crystalline magma when the hot solution is rapidly cooled; after a short time, the red salt changes into the yellow salt, and this change can be brought about many times with the same solution. The *calcium* salt, with  $8\text{H}_2\text{O}$ , obtained by adding calcium chloride to a saturated solution of the sodium salt, crystallises in orange-yellow prisms, and is easily soluble in water. It is converted into a red modification, with  $4\text{H}_2\text{O}$ , when heated with water on the water-bath; this crystallises in dark red leaflets, dissolves slowly in water, and then separates in the yellow modification.

*Dichloroplatiniooxalates.*—The *sodium* salt,  $\text{Na}_2\text{Cl}_2\text{Pt}(\text{C}_2\text{O}_4)_2 + 8\text{H}_2\text{O}$ , is obtained by treating a hot solution of sodium platino-oxalate with chlorine until a bright yellow solution is obtained, and then, without stopping the current of chlorine, concentrating on the water-bath; it separates in large, bright yellow crystals, is very soluble in water, decomposes on exposure to the air, and slightly explodes when heated. The *potassium* salt, with  $1\text{H}_2\text{O}$ , obtained in the same manner as the sodium salt, to which it is very similar, separates in prismatic crystals. The *calcium* salt, with  $6\text{H}_2\text{O}$ , obtained both from the red or yellow modification of the preceding calcium salt by the action of chlorine, separates in beautiful, dark yellow crystals, and is very soluble in water.

*Platiniplatino-oxalates.*—The *sodium* salt,  $\text{Pt}_5(\text{C}_2\text{O}_4)_{10}\text{Na}_8 + 20\text{H}_2\text{O}$ , obtained by treating a hot solution of sodium platino-oxalate with a small quantity of chlorine, crystallises in small prisms, is bright brown in transmitted light, has a beautiful, copper-bronze lustre, is stable on exposure to the air, and explodes when heated. The *potassium* salt, with  $12\text{H}_2\text{O}$ , is similar to the sodium salt, but of a brighter colour. The *calcium* salt, prepared from the red calcium platino-oxalate, forms dark brownish-red crystals having a faint bronze lustre, is stable on exposure to the air, and explodes on heating. The *salt* obtained from the yellow calcium platino-oxalate crystallises in small, yellowish-brown prisms. The results of the analysis gave numbers which did not conform to any probable formula. E. C. R.

**Formation of  $\beta$ -Bromalkylsuccinic Acids by Addition of Hydrogen Bromide to Homologues of Citraconic Acid.** By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 1070—1071; from *J. Russ. Chem. Soc.*, 1899, 31, 115—135).—In unsaturated monobasic acids, the position of the double linking in regard to that of the carboxyl group determines also the position of the bromine atom in the additive compounds formed with hydrogen bromide, and in the case of unsaturated dibasic

acids, if the double linking is between the carboxyl groups, a  $\beta$ -compound is formed, and in other cases a  $\gamma$ -compound.

*$\beta$ -Bromethylsuccinic acid*,  $\text{COOH}\cdot\text{CBrEt}\cdot\text{CH}_2\cdot\text{COOH}$ , prepared by the action of hydrobromic acid of sp. gr. 1.49 on methylcitraconic anhydride at  $0^\circ$ , separates in monoclinic crystals, melts at  $140\text{--}141^\circ$ , is easily soluble in ether, hot water, or chloroform, and less so in cold water or benzene. A small quantity of a bye-product was also isolated. The  $\alpha$ -compounds prepared by Bischoff (Abstr., 1891, 290, 1221) melt at  $111\text{--}116^\circ$  and at  $202.5^\circ$  respectively.  *$\beta$ -Bromethylsuccinic acid*, when decomposed with a small excess of sodium carbonate, yields  *$\alpha$ -ethylacrylic acid*,  $\text{CH}_2\cdot\text{CEt}\cdot\text{COOH}$ , which boils at  $179.5\text{--}180.5^\circ$  under 760 mm. pressure, and has a sp. gr. 1.0106 at  $0^\circ/0^\circ$ . The *calcium*, *barium*, and *silver* salts are described. When  *$\alpha$ -ethylacrylic acid* is cooled and treated with  $1\frac{1}{2}$  times the theoretical quantity of a 0.5 per cent. alkaline solution of potassium permanganate, it is instantly oxidised. The volatile portion of the product contains formic and propionic acids, whilst from the residue,  *$\alpha$ -ethylglyceric acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CEt}(\text{OH})\cdot\text{COOH}$ , may be isolated by means of its lead salt. This acid crystallises from ether in prisms, melts at  $99\text{--}100^\circ$ , is easily soluble in ether, and on further oxidation yields formic and propionic acids. The *lead* salt,  $(\text{C}_5\text{H}_9\text{O}_4)_2\text{Pb}$ , crystallises in square plates.

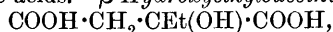
*$\beta$ -Bromopropylsuccinic acid*,  $\text{COOH}\cdot\text{CPrBr}\cdot\text{CH}_2\cdot\text{COOH}$ , prepared from ethylcitraconic anhydride, melts at  $122\text{--}123^\circ$ , and is soluble in water or chloroform. The aqueous solution appears to be supersaturated, and the peculiarity of the arrangement of the crystals which separate out from it is remarkable. When decomposed in alkaline solution, this acid forms  *$\alpha$ -propylacrylic acid*,  $\text{CH}_2\cdot\text{CPr}\cdot\text{COOH}$ , which boils at  $199^\circ$  under 745 mm. pressure and has a sp. gr. 0.9338 at  $0^\circ/0^\circ$ . The *calcium*, *barium*, and *silver* salts are described. When  *$\alpha$ -propylacrylic acid* is oxidised with potassium permanganate,  *$\alpha$ -propylglyceric acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CPr}(\text{OH})\cdot\text{COOH}$ , together with some formic and butyric acids, is formed.  *$\alpha$ -Propylglyceric acid* melts at  $94\text{--}95^\circ$ , and is soluble in ether. The *lead* salt crystallises in square plates.

*$\beta$ -Bromoisopropylsuccinic acid* may be prepared in a similar way to the preceding acid, and good yields of the crude acid, which melts and decomposes at  $152^\circ$ , are obtained. By the action of water at  $60\text{--}70^\circ$ , it yields a volatile acid which has an extremely unpleasant odour. The crude acid, when treated with sodium carbonate, yields  *$\alpha$ -isopropylacrylic acid*,  $\text{CH}_2\cdot\text{CPr}\cdot\text{COOH}$ , which boils at  $192.5\text{--}193^\circ$ , has a sp. gr. 0.9854 at  $0^\circ/0^\circ$ , and is slightly soluble in water. The *calcium* and *silver* salts are described. By oxidising with potassium permanganate, this acid yields  *$\alpha$ -isopropylglyceric acid*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CPr}(\text{OH})\cdot\text{COOH}$ , which melts at  $102\text{--}103^\circ$ , and is easily soluble in ether; some volatile acids are also formed.

E. W. W.

**Influence of Excess of Sodium Carbonate on the Decomposition of  $\beta$ -Bromalkylsuccinic Acids.** By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 1205; from *J. Russ. Chem. Soc.*, 1899, 31, 283—296. Compare preceding abstract).—The non-volatile acids obtained by decomposing  $\beta$ -bromalkylsuccinic acids with sodium carbonate, are found to be  $\beta$ -hydroxyalkylsuccinic acids, and the quantity produced is proportional

to the excess of sodium carbonate, this excess preventing the further decomposition of the acids. *β-Hydroxyethylsuccinic acid*,

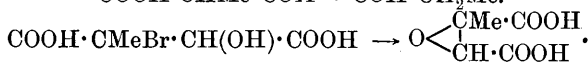
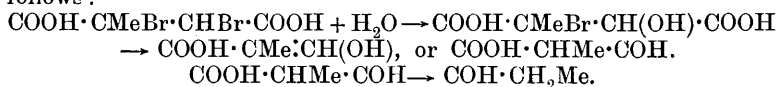


crystallises from alcohol in short prisms and melts at 131—133°. The *calcium* salt crystallises with 2H<sub>2</sub>O. *β-Hydroxypropylsuccinic acid*,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{C}^{\text{Pr}}(\text{OH}) \cdot \text{COOH}$ , separates from ether in thread-like crystals and melts at 127—128°. *β-Hydroxyisopropylsuccinic acid*,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{C}^{\text{Pr}^{\beta}}(\text{OH}) \cdot \text{COOH}$ , crystallises from ether in transparent, rectangular crystals and melts at 165—166°. Dimethylitaconic acid is also formed in the preparation of this acid, probably by the elimination of water. *Hydroxyppyrotartaric acid* is also obtained, together with metacrylic acid, when *β-bromopyrotartaric acid* is treated with an excess of sodium carbonate. This acid melts at 115—117°, and is rather sparingly soluble in ether. Mesoconic acid could not be detected in the products of this reaction.

The influence of conditions in regard to time, amount of excess of sodium carbonate, and concentration, are discussed in the original paper. The decomposition of dibromohydratropic acid by sodium carbonate shows that the excess of carbonate has also an important effect in this case.

E. W. W.

**Influence of Excess of Sodium Carbonate on the Decomposition of Dibromocitrapyrotartaric Acid.** By W. SSEMENOFF (*Chem. Centr.*, 1899, i, 1205—1206; from *J. Russ. Chem. Soc.*, 1899, 31, 296—305).—When dibromocitrapyrotartaric acid is decomposed in alkaline solution, hydrogen bromide, carbonic anhydride, bromometacrylic acid, and propaldehyde are formed (Fittig), but in the presence of an excess of sodium carbonate (10 mols.) the decomposition is limited, and, in addition to hydrogen bromide, carbonic anhydride, acetaldehyde, and bromometacrylic acid, a considerable quantity of hydroxycitraconic acid is obtained. The mechanism of this reaction is discussed in detail in the original paper, and is assumed to be as follows:



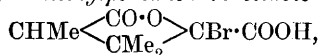
A similar decomposition occurs in the case of dibromohydratropic acid, *α*-hydroxy-*β*-bromohydratropic acid,  $\text{CH}_2\text{Br} \cdot \text{CPh}(\text{OH}) \cdot \text{COOH}$ , being first formed, and then decomposing into  $\text{CPh}(\text{OH}) \cdot \text{CH}_2 \rightarrow \text{Ph} \cdot \text{COMe}$ , or  $\text{CH}_2(\text{OH}) \cdot \text{CPh}(\text{OH}) \cdot \text{COOH}$ , according to the amount of the excess of sodium carbonate.

E. W. W.

**Oxidation Products of Camphoric Acid.** By LUIGI BALBIANO (*Real. Accad. dei Lincei*, 1899, 8, 422—427. Compare Abstr., 1895, i, 552, 678; 1897, i, 253).—By reducing the acid of the composition C<sub>8</sub>H<sub>12</sub>O<sub>5</sub>, which is the principal oxidation product of camphoric acid, *αβ*-trimethylglutaric acid and a lactonic acid are obtained; the author now shows the latter to be 3-dimethyl-4-methylpentane-2:5-olidic acid,  $\text{CHMe} \begin{array}{c} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{CMe}_2 \end{array} \text{CH} \cdot \text{COOH}.$

On heating the lactonic acid with hydriodic acid under pressure, it is converted into  $\alpha\beta$ -trimethylglutaric acid.

2-Bromo-3-dimethyl-4-methylpentane-2:5-olidic acid,



crystallises from benzene in groups of small, white, glistening prisms melting at 142–145°; it is decomposed by water with formation of hydrogen bromide. When heated with alkalis or barium hydroxide, it is converted into oxalic acid and another dibasic acid which crystallises in beautiful, glassy plates melting at 67–69°; it is either a hexamethyladipic acid,  $\text{C}_{12}\text{H}_{22}\text{O}_4$ , or a hexamethyltetramethylenedicarboxylic acid,  $\text{C}_{12}\text{H}_{20}\text{O}_4$ .

By acting on trimethylglutaric anhydride with bromine, *bromotrimethylglutaric anhydride* is obtained; when precipitated from a benzene solution by the gradual addition of light petroleum, it forms soft, white, sticky needles melting at 186–188°. It is very soluble in benzene, and almost insoluble in light petroleum. By treating this bromanhydride with alcohol, diethyl bromotrimethylglutarate is obtained together with another ethylic salt which, on decomposition with sulphuric acid, yields 3-dimethyl-4-methylpentane-2:5-olidic acid. This acid gives a *calcium* salt,  $(\text{C}_8\text{H}_{11}\text{O}_4)_2\text{Ca} + 2\text{H}_2\text{O}$ , which crystallises from water in small needles. The *lead* salt,  $(\text{C}_8\text{H}_{11}\text{O}_4)_2\text{Pb} + 2\text{H}_2\text{O}$ , crystallises in glistening, prismatic needles, soluble in water, and melting at 130–136°; the anhydrous salt softens at 168°, melts at 174°, and on cooling solidifies to a transparent, glassy mass.

T. H. P.

**Action of Tartaric and Citric Acids on Metallic Iron.** By KARL ULSCH (*Chem. Zeit.*, 1899, 23, 658. Compare this vol., ii, 802).—Aqueous solutions of both citric and tartaric acids act slowly on iron, liberating hydrogen. As the reaction is so slow, the volume of hydrogen given off with a mixture of  $N/10$  sulphuric and  $N/10$  tartaric acid was measured, a shaking apparatus being employed to accelerate the evolution of hydrogen. It was found that the amount evolved from the tartaric acid corresponded with the formation of the salt  $\text{Fe}_2\text{C}_4\text{H}_2\text{O}_6$ . Similarly, with citric acid, the amount of hydrogen agrees with the formation of the salt  $\text{Fe}_2\text{C}_6\text{H}_4\text{O}_7$ . In each case, therefore, not only the carboxylic hydrogen, but also the hydroxylic hydrogen had been replaced.

J. J. S.

**Alkali Copper Tartrates and Fehling's Solution.** By FRIEDRICH BULLNHEIMER and E. SEITZ (*Ber.*, 1899, 32, 2347–2352. Compare Masson and Steele, *Trans.*, 1899, 75, 725).—*Sodium copper ditartrate*,  $\text{C}_4\text{H}_2\text{O}_6\text{CuNa}_2 \cdot \text{C}_4\text{H}_2\text{O}_6\text{Na}_4 + 13\text{H}_2\text{O}$ , obtained by warming a mixture of tartaric acid, caustic soda, copper hydroxide, and water, filtering, shaking the filtrate with 96 per cent. alcohol, and allowing the lower layer which separates to crystallise in a desiccator, forms beautiful, light blue, deliquescent, monoclinic crystals, and dissolves in water with an alkaline reaction, is insoluble in alcohol, and is decomposed by heat. *Potassium copper ditartrate*,  $\text{C}_4\text{H}_2\text{O}_6\text{CuK}_2 \cdot \text{C}_4\text{H}_2\text{O}_6\text{K}_4 + 8\text{H}_2\text{O}$ , obtained similarly, forms harder crystals, and is darker in colour than the sodium compound.

On evaporating an aqueous solution of Rochelle salt, copper hydroxide, caustic potash, and caustic soda, two *sodium potassium copper ditartrates* separate; one of these,  $C_8H_4O_{12}CuNa_4K_2 + 11H_2O$ , closely resembles the sodium compound already described, whilst the other,  $C_8H_4O_{12}CuK_3Na_3 + 11H_2O$ , forms larger, monoclinic crystals of a deeper colour [ $a : b : c = 1.29 : 1 : 0.84$ ;  $\beta = 100^\circ 30'$ ]; the latter is more conveniently obtained by adding a mixture of methylic and ethylic alcohols to an aqueous solution of Rochelle salt, copper tartrate, caustic potash, and caustic soda.

Since 1 mol. of Rochelle salt in aqueous solution is capable of dissolving 1 mol. of copper hydroxide, it is usually assumed that there is present in Fehling's solution one or both of the compounds  $C_4H_2O_6CuNa_2$  or  $C_4H_2O_6CuKNa$ ; as, however, the compound  $C_4H_2O_6CuNa_2 + 2H_2O$ , which the authors have isolated by a method subsequently to be described, is decomposed on warming with water into copper oxide and sodium copper ditartrate, whereas Fehling's solution remains unchanged on heating, it is probable that the latter solution contains one or both of the ditartrates  $C_8H_4O_{12}CuK_2Na_4 + 11H_2O$ , or  $C_8H_4O_{12}CuK_3Na_3 + 11H_2O$ .

On dissolving copper tartrate in concentrated aqueous ammonia, adding alcohol, and cooling to  $0^\circ$ , dark blue crystals of *cupritetrammonium tartrate*,  $C_4H_4O_6Cu(NH_3)_4 + 2H_2O$ , separate; *copper cupritetrammonium tartrate*,  $C_4H_2CuO_6Cu(NH_3)_4$ , is obtained similarly from a solution of ammonium tartrate, copper hydroxide, and aqueous ammonia.

W. A. D.

**Hydroxygluconic Acid.** By OTTO RUFF (*Ber.*, 1899, 32, 2269—2273).—In the preparation of *d*-arabinose by the oxidation of calcium gluconate, the calcium and iron salts which remain after the separation of this substance show marked reducing properties, and contain appreciable quantities of calcium hydroxygluconate, which, owing to its insolubility, can be readily isolated. Hydroxygluconic acid,  $OH \cdot CH_2 \cdot CO \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot COOH$ , is identical with the compound obtained by Boutroux (*Abstr.*, 1890, 1399) by the bacterial fermentation of calcium gluconate, but differs from the hydroxygluconic acid described by W. Tiemann (*Zeit. Verein Rübenzuck-Ind.*, 40, 787), as being formed when calcium gluconate is oxidised with bromine. The latter substance, however, seems to be gluconic acid containing a small quantity of hydroxyketonic acids; Tiemann's potassium salt was potassium gluconate and his osazone, *gluconic acid phenylhydrazide*, a substance separating from methylic alcohol in prisms and melting at  $200^\circ$ .

J. F. T.

**Preparation of Monobasic Acids of the Sugar Group.** By OTTO RUFF (*Ber.*, 1899, 32, 2273—2274).—The great drawback to Kiliani's process for the preparation of large quantities of monobasic acids of the sugar group is the loss of bromine which occurs during the reaction. The author finds that an equally good yield of these acids is obtained when only a little more than the theoretical quantity of bromine is used.

J. F. T.

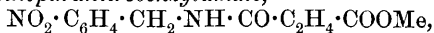
**Condensation of Glutaconic Acid.** By HANS VON PECHMANN (*Ber.*, 1899, 32, 2301).—When acted on by ethylic formate, two

molecules of ethylic glutaconate condense to form a *polymeric* etheric salt, which forms a thick oil and boils at  $224^{\circ}$  under 22 mm. pressure. The polymeric acid,  $C_{10}H_{12}O_8$ , crystallises in white prisms, and melts and decomposes at  $207^{\circ}$ . T. M. L.

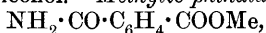
**Action of Methylic Alcohol on Imides of Dibasic Acids.** By SEBASTIAAN HOOGEWERFF and WILLEM ARNE VAN DORP (*Rec. Trav. Chim.*, 1899, **18**, 358—366. Compare Abstr., 1898, i, 589).—*Methylic succinamate*,  $NH_2 \cdot CO \cdot C_2H_4 \cdot COOMe$ , obtained by heating succinimide with 8 parts of methylic alcohol at  $170^{\circ}$  for 3 hours, crystallises from a mixture of acetone and ether in nacreous plates melting at  $89-91^{\circ}$ ; it is readily soluble in water and the ordinary organic solvents; it may also be prepared by heating silver succinamate with methylic iodide.

*Succinoparanitrobenzylimide*, prepared by heating an alcoholic solution of succinimide, paranitrobenzyl chloride, and caustic soda, crystallises from alcohol in colourless plates and melts at  $150-152^{\circ}$ .

*Methylic succinoparanitrobenzylamate*,



produced by heating the preceding compound with methylic alcohol at  $170^{\circ}$ , crystallises from benzene in colourless needles melting at  $116-118.5^{\circ}$ . When heated at  $170^{\circ}$  with excess of alcohol, this substance is partially reconverted into the imide; the reaction (imide + MeOH = methylic amido-ester) appears to be a reversible one. The methylic salts of maleamic, phthalophenylamic, and orthosulphamidobenzoic acids can also be prepared by heating the corresponding imides with methylic alcohol. *Methylic phthalamate*,



could not be obtained by this method, but is produced by heating silver phthalamate with methylic iodide dissolved in acetone; it melts at  $98-102^{\circ}$ , and when heated to  $140^{\circ}$  decomposes into phthalimide and methylic alcohol. G. T. M.

**Methyleneasparagine.** By HUGO SCHIFF (*Chem. Zeit.*, 1899, **23**, 20—21).—*Methyleneasparagine*,  $COOH \cdot CH(N \cdot CH_2) \cdot CH_2 \cdot CO \cdot NH_2$ , is obtained when the requisite quantity of asparagine is dissolved in slightly warm 20 per cent. formaldehyde solution and the syrupy product allowed to crystallise; it may also be obtained by cooling a solution of asparagine in hot water to  $40-45^{\circ}$  and then adding the requisite quantity of 40 per cent. formaldehyde. It crystallises in colourless plates or nodular masses, dissolves readily in warm water, and has a strong tendency to form supersaturated solutions; its aqueous solution has a decidedly acid reaction, is highly lavo-rotatory, and does not give the biuret reaction. The *copper* salt,  $(C_5H_7O_3N_2)_2Cu + 5H_2O$ , crystallises in dark blue needles; neither the acid nor its salts lose formaldehyde when exposed to the air.

*Dimethyleneasparagine*, probably identical with the compounds described by Goldschmidt (*Chem. Zeit.*, 1898, **22**, 374), is obtained when finely powdered asparagine (1 mol.) is dissolved in warm 25—30 per cent. formaldehyde (3 mols.). It forms a fine powder, and in a moist condition readily gives up formaldehyde when exposed to the air, the product left being methyleneasparagine. Two sparingly soluble *copper*



salts,  $(C_6H_7N_2O_3)_2Cu + 1\frac{1}{2}H_2O$  and  $C_5H_7N_2O_3 \cdot Cu \cdot C_6H_7N_2O_3 + H_2O$ , have been prepared. J. J. S.

**Alkyl diazourethanes (so-called Nitrosoalkylurethanes).** By JULIUS W. BRÜHL (*Ber.*, 1899, 32, 2177—2178).—Hantzsch (this vol., i, 686) assigns to nitrosourethane and its methyl derivative the diazo-formulae  $COOEt \cdot N:N \cdot OH$  and  $COOEt \cdot N:N \cdot OMe$ , and to the isomeride of the latter, which is obtained by the action of nitrous acid on methylurethane, the formula  $COOEt \cdot NMe \cdot NO$ . As regards the first point, the author some time ago (*Abstr.*, 1897, i, 339) assigned the formula  $COOEt \cdot N:N \cdot OEt$  to the ethyl derivative of nitrosourethane; he has also given reasons (*Abstr.*, 1898, ii, 362) for assigning to the isomeride, not the constitution suggested by Hantzsch, but a diazo-structure, as expressed by the formula  $COOEt \cdot NR \begin{smallmatrix} \text{N} \\ \diagup \\ \text{O} \end{smallmatrix}$ . C. F. B.

**Action of Argon and Nitrogen on Mercury Methyl and Mercury Phenyl.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 378—379).—When a silent electric discharge is passed through argon in the presence of mercury dimethyl, the mercuric compound is decomposed, but argon is not absorbed and no luminosity is produced; if, however, mercury diphenyl is substituted for the mercury dimethyl, a green luminosity is produced, which, on account of the low vapour pressure of the mercuric compound, is not very intense. After the silent discharge has been acting for 41 hours, there is an absorption of argon equal to 8.9 per cent. of the gas taken. When a silent electric discharge is passed through nitrogen in the presence of mercury dimethyl, there is an absorption of nitrogen and the condensed substance has the composition  $C_2H_{3.4}N_{0.50}$ . H. R. LE S.

**Preparation of Organo-Zinc Compounds and Synthesis of Hexane.** By L. SIMONOWITSCH (*Chem. Centr.*, 1899, i, 1066; from *J. Russ. Chem. Soc.*, 1899, 31, 38—42).—A 92 per cent. yield of zinc ethyl is obtained by gradually heating a mixture of equal weights of dry ethylic iodide and zinc dust from 80° to 96°. Zinc dust is previously treated with acid and dried in carbonic anhydride at 160—180°, and zinc shavings are added to the mixture in quantity sufficient for a portion to project from the surface of the liquid. When all the ethylic iodide has disappeared, the product is distilled. The whole process requires only 1½—2 hours. For the preparation of zinc methyl, Ipatieff's method (*J. Russ. Chem. Soc.*, 27, 364) is recommended, zinc dust being used, however, instead of zinc shavings. By the action of isobutylic iodide on zinc ethyl iodide,  $ZnEtI$ , at 95°, ethylene, isobutylene, and a hexane boiling at 47.5—50°, and hence probably trimethylpropane, are formed. The sp. gr. of the last compound is 0.7305 at 0°. E. W. W.

**Preparation of Zinc Methyl.** By W. WOROBEEFF (*Chem. Centr.*, 1899, i, 1067; from *J. Russ. Chem. Soc.*, 1899, 31, 45—46).—When methylic iodide is heated with zinc dust and zinc shavings in an iron

vessel, the reaction takes place more quickly, but the yield of zinc methyl is reduced from 87 (Ipatieff, *J. Russ. Chem. Soc.*, 27, 364) to 78 per cent. E. W. W.

**Preparation of Zinc Isopropyl.** By J. BOHM (*Chem. Centr.*, 1899, i, 1067; from *J. Russ. Chem. Soc.*, 1899, 31, 46—47).—A 25 per cent. yield of zinc isopropyl which boils at 135° is obtained by Simonowitsch's method (preceding abstracts), the mixture being kept at 40°. The product decomposes when distilled, with evolution of gas and fumes of zinc oxide. E. W. W.

**Acetylthiophenine [Acetamidothiophen].** By ENRICO RIMINI (*Chem. Zeit.*, 1899, 23, 266).—Acetylthiophen ketoxime is readily converted by the Beckmann reaction into *acetamidothiophen*,  $C_4H_3S \cdot NHAc$ . The molecular rearrangement is best brought about by dissolving the oxime in dry ether, cooling with a freezing mixture, adding phosphorus pentachloride until the reaction ceases, washing the ethereal solution with water, and finally crystallising the product from alcohol. In appearance, it resembles acetanilide. J. J. S.

**Trimethylene.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 483—491).—The action of bromine on propylene in presence of water is much more rapid than on trimethylene, and affords a means of purifying the latter, which, however, is slowly affected, and if sufficient time is allowed, is also completely absorbed. The difference between the rates of action is sufficient to permit of the use of bromine for the approximate analysis of a mixture of the two gases.

When propylic or isopropylic alcohol is heated with zinc chloride, the product is mainly propylene mixed with small quantities of propane, hydrogen, and liquid hydrocarbons, but no trimethylene. Similar results are obtained with concentrated sulphuric acid.

Trimethylene, when heated with zinc chloride at its melting point, is gradually converted into propylene; when heated alone, it is almost completely converted into propylene, mixed with some paraffins, ethylene, and hydrogen. Propylenic bromide is very rapidly attacked by zinc in presence of alcohol at the ordinary temperature, whereas a temperature of 60—70° is required in the case of trimethylenic bromide, the liberated trimethylene being partly converted into propylene.

These facts illustrate the relative instability of trimethylene, and are in accordance with thermochemical data. C. H. B.

**Cyclic Acetone Bases.** By HERMANN PAULY (*Ber.*, 1899, 32, 2244).—Triacetoneamine is formed when diacetoneamine oxalate is boiled with acetone, but this method is not suitable for its preparation. Guareschi's reaction, on the other hand, can not only be applied to the preparation of triacetoneamine itself, but also to that of other acetone bases. Thus benzylidenemesityl oxide,  $CHPh \cdot CH \cdot CO \cdot CH \cdot CMe_2$ , is converted by aqueous ammonia into benzylidenediacetoneamine,  $CO < \begin{smallmatrix} CH_2 - CMe_2 \\ CH_2 \cdot CHPh \end{smallmatrix} > NH$ . A. H.

[Theory of] Unsaturated and Aromatic Compounds. By JULIUS W. BRÜHL (*Annalen*, 1899, 308, 203—212. Compare Thiele, this vol., i, 554).—The author criticises Thiele's discussion of the constitution of unsaturated compounds and of benzene (*loc. cit.*), and fails to recognise an essential difference between his previously expressed views and those now put forward by Thiele. M. O. F.

Constitution of Benzene. By JOHANNES THIELE (*Annalen*, 1899, 308, 213—217. Compare this vol., i, 554).—A reply to the foregoing paper by Brühl. M. O. F.

Nitrating Action of Nitric Acid on Saturated Hydrocarbons. VII. Nitration of Methylbenzenes. By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 1237—1239; from *J. Russ. Chem. Soc.*, 1899, 31, 254—273).—The results obtained by the action of nitric acid on toluene, meta- and para-xylene, mesitylene, and tertiary butyltoluene under different conditions are given in tables in the original paper. Toluene gives the best yield of nitro-derivatives containing the nitro-group in the side-chain, when heated with acid of sp. gr. 1.12 for 48 hours at 100° in a sealed tube. Metaxylene, paraxylene, and mesitylene may be nitrated by acid of sp. gr. 1.075, either in open or closed vessels, the first compound requiring the most time and mesitylene the least. The best yield of nitro-derivatives of butyltoluene is obtained by heating with acid of sp. gr. 1.075 at 105°. The nitro-compounds were purified by conversion into the sodium derivatives, and then decomposing these with carbonic anhydride or boric acid.

Phenylnitromethane [ $\omega$ -nitrotoluene] boils at 141—142° under 35 mm. pressure, boils and decomposes at 225—227° under the ordinary pressure, has a sp. gr. 1.1756 at 0°/0°, 1.1598 at 20°/0°, and a specific refractive index  $[n]_D$  1.53230 at 20°. The alkali salts give the nitrolic acid reaction, yield isophenylnitromethane when treated with strong acids, and benzylamine when reduced with tin and hydrochloric acid. Metatoluenenitromethane [ $\omega$ -nitrometaxylene],  $C_6H_4Me \cdot CH_2 \cdot NO_2$ , is a yellowish liquid which boils and decomposes at 140° under 35 mm. pressure, and has a sp. gr. 1.1370 at 0°/0° and 1.1197 at 20°/0°. By allowing it to remain with calcium chloride, metatoluic acid is formed. The potassium derivative of  $\omega$ -nitrometaxylene crystallises in yellow leaflets. The sodium derivative is prepared by means of sodium ethoxide, and is a white powder. The calcium, barium, and strontium derivatives are white, stable powders. Metaxylylamine,  $C_6H_4Me \cdot CH_2 \cdot NH_2$ , boils at 205—205.5° under 750.5 mm. pressure, and has a sp. gr. 0.9809 at 0°/0° and 0.9654 at 20°/0°. The hydrochloride forms small crystals and melts and decomposes at 181—191°. The sulphate crystallises in large plates and melts at 250°. The platinochloride is insoluble in alcohol or ether, and melts at 198—200°; the aurichloride crystallises in leaflets containing  $1H_2O$ , and is soluble in water. Paratoluenenitromethane [ $\omega$ -nitroparaxylene] melts at 11—12°, has a sp. gr. 1.1234 at 20°/0°, specific refractive index  $[n]_D$  = 1.53106 at 20°, boils with slight decomposition at 150—151° under 35 mm. pressure, gives the nitrolic acid reaction in alkaline solutions, and decomposes into paratoluic acid. Several metallic derivatives are described. Paraxylylamine melts at

12.6—13.2°, boils at 204° under 739 mm. pressure, has a sp. gr. 0.9520 at 20°/0°, 0.9501 at 30°/0°, a specific refractive index 1.53639 at 20°, and rapidly absorbs carbonic anhydride from the air. *Metaxylenemetanitromethane* [ $\omega$ -nitromesitylene],  $C_6H_3Me_2 \cdot CH_2 \cdot NO_2$  [ $Me_2 : CH_2 \cdot NO_2 = 1 : 3 : 5$ ], crystallises in large plates, melts at 46—47°, boils and decomposes at 120—170° under 25 mm. pressure, forming mesitylenic acid and mesitylaldehyde, and other compounds. The alkali derivatives are soluble in water or alcohol, give the nitrolic acid reaction, are precipitated by metallic salts, and when treated with nitric acid of sp. gr. 1.155 yield mesitylenic acid.  $\omega$ -Mesitylamine,  $C_6H_3Me_2 \cdot CH_2 \cdot NH_2$  [ $Me_2 : CH_2 \cdot NH_2 = 1 : 3 : 5$ ], boils at 220—221° under 758 mm. pressure, has a sp. gr. 0.9631 at 0°/0°, 0.9500 at 20.5°/0°, specific refractive index 1.53046 at 20.5°, absorbs carbonic anhydride from the air with avidity, and is identical with Landau's compound (Abstr., 1893, i, 32). The hydrochloride crystallises in prisms, melts at 245—246°; the nitrate forms prisms and melts at 170°. 1-Nitromethyl-2-nitro-3:5-dimethylbenzene [ $\omega$ :2-dinitromesitylene],  $NO_2 \cdot CH_2 \cdot C_6HMe_2(NO_2)_2$ , prepared by further nitrating  $\omega$ -nitromesitylene at -10° with nitric acid of sp. gr. 1.48, melts at 85.5—86°. The alkali salts are easily soluble in water, forming orange-red solutions, from which carbonic anhydride precipitates the original substance, and dilute sulphuric acid the isodinitro-compound.  $\omega$ :2-Dinitromesitylene, when oxidised by a 4 per cent. solution of potassium permanganate, yields orthonitromesitylenic acid, which melts at 210—212°. By the action of nitric acid of sp. gr. 1.51 on the original mononitro-compound or on the dinitro-compound, a mixture of crystalline compounds is formed, from which a trinitro-derivative,  $C_9H_9(NO_2)_3$ , may be isolated. This substance melts at 117.5—118.5°, is easily soluble in benzene, ether, or chloroform, and yields alkali salts, from which, by the action of carbonic anhydride, or of dilute sulphuric acid, the original compound is regenerated; an isonitro-compound could not be obtained.

The heats of combustion per gram-molecule and the melting points of the following isomeric nitromesitylenes are quoted :

	Melting point.	Heat of combustion.
$C_6H_2Me_3(NO_2)$ .....	44°	1,216,660 Cal.
$C_6H_3Me_2 \cdot CH_2 \cdot NO_2$ .....	46—47°	1,206,332 „
$C_6HMe_3(NO_2)_2$ .....	86—87°	1,186,710 „
$C_6H_2Me_2(NO_2)_2 \cdot CH_2 \cdot NO_2$ [ $= 1 : 3 : 4 : 5$ ] .....	85.5—86°	1,165,857 „

In each case, the heat of combustion of the derivative containing the nitro-group in the side-chain is less than that of its isomeride containing this group in the benzene ring. E. W. W.

**Simple Method of Etherification of Phenols and Aldehydes by means of an Acid Radicle and Quick Method of Acetylation of Aromatic Amines containing Negative Groups.** By GEORGES FREYSS (*Chem. Centr.*, 1899, i, 835—836; from *Bull. Soc. ind. Mulhouse*, 1899, 44—48).—Valeraldehyde is only attacked by acetic anhydride when it is heated with it under pressure at a high temperature, but when a drop of concentrated sulphuric acid is added to the mixture,

an energetic reaction takes place at the ordinary temperature; in like manner, a good yield of acetyl derivatives of many aldehydes, hydroxyaldehydes, phenols, substituted phenols containing negative groups, and polyhydric alcohols may be obtained. Amines containing one or more negative groups, amidophenols, &c., also yield large quantities of acetyl derivatives, but the preparation of mixed ketones from ethers of phenols, or of the hydrocarbons,  $C_nH_{2n-6}$ , by means of acetic anhydride and sulphuric acid is less satisfactory. Acetates were prepared in this way from phenol, guaiacol (the acetate is a liquid with a strong aromatic odour boiling at  $239-241^\circ$  under 738 mm. pressure), eugenol (the acetate is a liquid boiling at  $278-279^\circ$  under 750 mm. pressure), and orthonitrophenol. Diacetates from resorcinol, benzaldehyde, and parachlorometanitrobenzaldehyde (the salt forms yellowish, lustrous crystals melting at  $97^\circ$ ), and mono- and triacetates from salicylaldehyde and of vanillin have also been prepared. E. W. W.

**Reactions of Phenyl Chlorocarbonates.** By ALBERT MOREL (*Bull. Soc. Chim.*, 1899, [iii], 21, 815—823, 823—830. Compare this vol., i, 586, 747).—The phenyl chlorocarbonates are decomposed by water, very slowly at the ordinary temperature, but immediately at  $100^\circ$ , with formation of normal phenyl carbonates and the products of decomposition of carbonyl chloride. Similar decompositions are effected by the action of aqueous alkalis and solutions of basic lead acetate, silver nitrate, &c. With alkali alkyloxides, a mixture of normal phenyl and alkyl carbonates is obtained. Aliphatic alcohols have little or no action on phenyl chlorocarbonates in the cold, even in the presence of aluminium chloride, but on heating, the theoretical amount of hydrogen chloride is evolved, and excellent yields of mixed phenyl alkyl carbonates are obtained. The temperature required to bring about this reaction depends on the molecular weight and the constitution of the alcohol employed, and has been experimentally determined in the case of methyl (66°), ethyl (78°), normal and propyl (90°), butyl (103°), heptyl (142°), octyl (155°), and benzyl (160°) alcohols, and also for isopropyl (86°), isobutyl (99°), ordinary amyl (111°), and allyl (92°) alcohols. Better yields are obtained with alcohols requiring high than with those requiring low temperatures. The following compounds have been prepared by the method described.

*Phenyl butyl carbonate* is a colourless liquid boiling at  $129-130^\circ$  under 25 mm. pressure, has a sp. gr. 1.0507 at  $0^\circ$ , and a refractive index 1.47951 at  $16.1^\circ$ . *Phenyl heptyl carbonate* is a colourless liquid which boils at  $136^\circ$  under 25 mm. pressure, and has a sp. gr. 1.0465 at  $0^\circ$  and refractive index 1.47812 at  $16.1^\circ$ . *Phenyl octyl carbonate* is a colourless liquid boiling at  $145^\circ$  under 30 mm. pressure; it has a sp. gr. 1.0432 at  $0^\circ$ , and a refractive index 1.47647 at  $16.1^\circ$ . *Phenyl capryl carbonate* is a colourless liquid boiling at  $142-145^\circ$  under 30 mm. pressure, has a sp. gr. 1.0492 at  $0^\circ$ , and a refractive index 1.48224 at  $15.7^\circ$ . *Phenyl benzyl carbonate* is a faintly yellow liquid which boils at  $180-190^\circ$  under 30 mm. pressure, has a sp. gr. 1.1366 at  $0^\circ$ , and a refractive index 1.49141 at  $15.7^\circ$ .

Orthotolyl ethyl carbonate, a colourless liquid, boils at  $132^\circ$  under

30 mm. pressure, has a sp. gr. 1.1271 at 0°, and a refractive index 1.49399 at 15.7°. Metatolylic ethylic carbonate is a colourless liquid boiling at 135—138° under 30 mm. pressure; it has a sp. gr. 1.1351 at 0° and a refractive index 1.49522 at 15.7°. Paratolylic ethylic carbonate is a colourless liquid which boils at 138—140° under 30 mm. pressure, has a sp. gr. 1.1389 at 0°, and a refractive index 1.49647 at 15.7°. This and the two preceding compounds are identical with those which Bender obtained by the action of ethylic chlorocarbonate on the three sodium tolyloxides.

*Parachlorophenylic ethylic carbonate* is a colourless liquid which boils at 135—145° under 30 mm. pressure, has a sp. gr. 1.1726 at 0°, and a refractive index 1.51700 at 15.7°.

Thymylic ethylic carbonate, a colourless liquid which boils at 145—154° under 25 mm. pressure, has a sp. gr. 1.1524 at 0°, and a refractive index 1.49981 at 15.7°; it has been prepared by Richter by treating ethylic chlorocarbonate with sodium thymyloxide.

The specific gravity of the mixed phenylic alkylic carbonates decreases as the molecular weight increases, at least for the series of normal alcohols, and the following measurements, together with those already quoted, show that a similar relation holds good for the indices of refraction. The numbers refer to the D-line at 15.7—16.1°; air temperature = 20°. Phenylic methylic carbonate, 1.50221; phenylic ethylic carbonate, 1.49093; phenylic propylic carbonate, 1.48640; phenylic isopropylic carbonate, 1.48429; phenylic isobutylic carbonate, 1.47334; phenylic isoamylic carbonate, 1.47768; phenylic allylic carbonate, 1.50258; guaiacylic methylic carbonate, 1.51736; guaiacylic ethylic carbonate, 1.50297; guaiacylic propylic carbonate, 1.49872; guaiacylic isobutylic carbonate, 1.46781; guaiacylic isoamylic carbonate, 1.47087; guaiacylic benzylic carbonate, 1.49265.

The second paper deals with the action of phenylic chlorocarbonates on phenols and on organic bases. Phenylic chlorocarbonates have no action on phenols in the cold, even in the presence of aluminium chloride, and, on heating, the only reaction which occurs is the decomposition of the chlorocarbonate with the formation of carbonyl chloride and normal phenylic carbonate. A similar decomposition takes place with anhydrous alkali phenyloxides, but by gradually adding a concentrated solution of the phenol in aqueous soda to a solution of the chlorocarbonate in benzene or ether, mixed phenylic carbonates are readily obtained. *Phenylic paratolylic carbonate*, prepared in this way from phenylic chlorocarbonate and sodium tolyloxide, crystallises in slender, colourless needles melting at 94°. *Phenylic guaiacylic carbonate* melts at 82°, *phenylic parachlorophenylic carbonate* at 92°, *guaiacylic parachlorophenylic carbonate* at 98°, and *guaiacylic paracresylic carbonate* at 99°.

Phenylic chlorocarbonates interact readily with ammonia in alcoholic solution, and phenylic, guaiacylic, tolylic, thymylic, and parachlorophenylic carbamates, all of which have been obtained by other methods and previously described, were prepared in this way. The following substituted carbamates were obtained in a similar manner by the action of primary and secondary amines. Phenylic phenylcarbamate, which Hofmann obtained by heating phenylic cyanate with phenol, crystallises

in slender, colourless needles melting at  $125.5^{\circ}$ . *Guaiacylic phenyl-carbamate* crystallises in slender, colourless needles, and melts at  $136^{\circ}$ . *Phenylic phenylcarbamate*, from phenylhydrazine and phenylic chlorocarbonate, crystallises in small needles melting at  $122-123^{\circ}$ , decomposes at  $200^{\circ}$ , and has strong reducing properties. All these compounds are insoluble in cold, and almost insoluble in hot, water, but soluble in all organic solvents. They crystallise well from chloroform, and are insoluble in dilute acids. *Phenylic dipropylcarbamate* is a liquid which boils at  $168^{\circ}$  under 30 mm. pressure.

When phenylic chlorocarbonate and pyridine are mixed in alcoholic or ethereal solution, considerable heat is developed, probably due to the formation of an unstable additive product which decomposes into normal phenylic carbonate and a compound of pyridine with carbonyl chloride. The latter compound, which is also obtained as a yellowish-white precipitate by the direct action of pyridine on carbonyl chloride in toluene solution, appears to have the composition  $\text{COCl}_2(\text{C}_5\text{H}_5\text{N})_2$ , and is very unstable. N. L.

**Constitution of Dichlororthocresol.** By C. MARTINI (*Gazzetta*, 1899, 29, ii, 60—64).—The dichlororthocresol obtained by the action of sulphuryl chloride (2 mols.) on orthocresol (1 mol.) is identical with the compound melting at  $55^{\circ}$  prepared by Claus and Riemann (*Abstr.*, 1883, 1111) by the direct action of chlorine.

*Dichlororthomethoxytoluene*,  $\text{C}_6\text{Cl}_2\text{H}_2\text{Me}\cdot\text{OMe}$ , obtained by the action of potassium hydroxide and methylic iodide on dichlororthocresol, melts at  $29-30^{\circ}$ , and on cooling remains liquid (even if shaken) until a temperature of  $17^{\circ}$  is reached, when it suddenly solidifies to a radiating mass of long prisms resembling menthol. It has an aromatic odour, and is very soluble in ether, alcohol, benzene, or light petroleum, its solutions exhibiting supersaturation. On oxidation with nitric acid, it yields the methylic derivative of dichlorosalicylic acid (*dichlororthomethoxybenzoic acid*),  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{COOH}$ , which crystallises from dilute alcohol in long, white, prismatic needles, sublimes with partial decomposition, and melts at  $165.5-167^{\circ}$ . The dichlorosalicylic acid obtained by the action of hydriodic acid on this compound melts at  $219.5^{\circ}$ , and is found to be identical with the 3:5-dichlorosalicylic acid described by Lössner and by Smith as melting at  $214^{\circ}$ , and by Zincke as melting at  $219^{\circ}$ .

It is concluded that the dichlororthocresol melting at  $55^{\circ}$  has the constitution  $[\text{Me} : \text{OH} : \text{Cl} : \text{Cl} = 1 : 2 : 3 : 5]$ . T. H. P.

**Constitution of Dichloroparacresol.** By V. BERTOZZI (*Gazzetta*, 1899, 29, ii, 35—41).—*Dichloroparamethoxytoluene*,  $\text{C}_6\text{H}_2\text{Cl}_2\text{Me}\cdot\text{OMe}$ , obtained by the action of methylic iodide and a methylic alcohol solution of potassium hydroxide on dichloroparacresol, is a colourless oil boiling at  $234^{\circ}$ . On oxidation with nitric acid, it yields dichloranisic acid, which crystallises from alcohol in large, white, shining needles melting at  $200-201^{\circ}$ , and is identical with the acid obtained by Reinecke by treating anisic acid with hydrochloric acid and potassium chlorate; Reinecke gave the melting point  $196^{\circ}$ . With hydriodic acid, dichloranisic acid yields an acid forming small, acicular crystals melting at  $265^{\circ}$ , which proves to be identical with dichlorohydroxybenzoic acid

[Cl : Cl : OH : COOH = 3 : 5 : 4 : 1], the melting point of which was given by Lössner as 255—256°, and by Zincke as 259—260°.

*Benzoyldichloroparacresol*,  $C_6H_2Cl_2Me \cdot OBz$ , crystallises from light petroleum in large, monoclinic prisms melting at 89°.

It is concluded that dichloroparacresol has the constitution  
[Me : Cl : Cl : OH = 1 : 3 : 5 : 4]. T. H. P.

**Action of Ether and Aluminium Chloride on Aromatic Hydrocarbons.** By PAUL JANNASCH and A. RATHJEN (*Ber.*, 1899, 32, 2391—2394. Compare Abstr., 1898, i, 565).—*Diethylphenol*,  $C_6H_3Et_2 \cdot OH$  [1 : 3 : 5], is made by heating phenol, ethylic ether, and aluminium chloride at 145°. It has a characteristic phenolic odour, dissolves sparingly in water but readily in alcohol, ether, benzene, or chloroform, crystallises from light petroleum in long, shining needles or large, compact prisms, melts at 77°, and boils at 239°. It dissolves readily in dilute soda and is reprecipitated by carbonic anhydride; its dilute alcoholic solution gives no coloration with ferric chloride. *Tribromodiethylphenol*,  $C_6Et_2Br_3 \cdot OH$ , separates from acetic acid in silky needles melting at 128°. *Trinitrodiethylphenol*,  $C_6Et_2(NO_2)_3 \cdot OH$ , separates from light petroleum in yellow leaflets or in magnificent, transparent rhombohedra, melts at 91°; is sparingly soluble in water, and dissolves readily in alcohol, ether, or benzene; with aniline, it gives a compound crystallising in golden-yellow needles.

*Tetrethylphenol*,  $C_6H_2Et_4 \cdot OH$ , formed when more ether and aluminium chloride is used than in the foregoing case, is very readily soluble in the usual media with the exception of water; it is obtained in long needles by leading hydrogen chloride in the alcoholic solution. It melts at 45° and boils at 270—271°.

*Hydroxydiethylbenzaldehyde*,  $OH \cdot C_6H_2Et_2 \cdot CHO$ , prepared from diethylphenol by the Gattermann reaction, is less readily soluble than diethylphenol in most media, and crystallises from boiling light petroleum in slender needles melting at 107°. The production of this aldehyde indicates that in diethylphenol the para-position is occupied by hydrogen, and the authors suggest that the compound has the constitution [CHO : Et<sub>2</sub> : OH = 1 : 2 : 6 : 4].

The foregoing method of ethylation is regarded as a valuable one, the yield of product being usually very high. A. L.

**Electrolytic Conductivity of Hydroresorcinols and δ-Ketonic Acids.** By RUDOLF VON SCHILLING and DANIEL VORLÄNDER (*Annalen*, 1899, 308, 184—202).—The acidic properties of hydroresorcinols are as strongly marked as those of δ-ketonic acids, although the carboxyl group is absent. The structural difference between the two classes of compounds does not amount to much more than ring-formation, as may be seen by comparing hydroresorcinol,  $CH_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{CH}$ , with γ-acetobutyric acid,  $CH_2 \begin{smallmatrix} \text{CH}_2 \text{---} \text{CO} \\ \text{CH}_2 \cdot \text{COOH} \end{smallmatrix} \text{CH}_3$ , and cyclic, organic substances containing oxygen usually exhibit acidic properties more pronounced than those open-chain compounds of similar constitution; for instance, hydroresorcinol may be titrated with caustic alkali and phenolphthalein, whilst acetylacetone,  $CH_3 \cdot CO \cdot CH : C(\text{OH}) \cdot CH_3$ , gives no



definite end-point, and comparison of the first-named substance with ethylic  $\beta$ -keto-hexamethylenecarboxylate,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CH}_2 \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{C} \cdot \text{COOEt}$ , indicates that the acidic influence of the carbonyl group of the ring is more powerful than that of the carbonyl radicle.

The authors have determined the electrolytic conductivity of certain hydroresorcinol derivatives and  $\delta$ -ketonic acids, in order to ascertain which group of compounds is the more powerfully acidic. The results are summarised in the following table:

$\delta$ -Ketonic acids.	<i>K</i> .	Hydroresorcinol derivatives.	<i>K</i> .
$\gamma$ -Acetobutyric .....	0·0022	Hydroresorcinol .....	0·00055
$\beta$ -Methyl- $\gamma$ -acetobutyric .....	0·0027	Methylhydroresorcinol .....	0·00057
$\beta$ -Phenyl- $\gamma$ -acetobutyric .....	0·0032	Dimethylhydroresorcinol .....	0·00071
$\beta$ -Phenyl- $\gamma$ -trimethacetobutyric .....	0·0025	Phenylhydroresorcinol .....	0·0012
		Furylhydroresorcinol.....	0·0015
		Ethylic methylhydroresorcy- late .....	0·0037
		Methylic dimethylhydroresor- cyate .....	0·0048
		Ethylic phenylhydroresorcy- late .....	0·0061
		Phenylhydroresorcylic nitrile.	0·0019
		Phenylmethylhydroresorcylic nitrile .....	0·020

From this it appears that the  $\delta$ -ketonic acids are 3—5 times stronger than the corresponding hydroresorcinols, and it becomes possible to distinguish these groups by conductivity determinations. The  $\delta$ -ketonic acids cannot, however, be distinguished from the hydroresorcylic esters and nitriles by this means.

Conversion into a cyclic compound increases the acidity of acetyl-acetone ( $K = 0\cdot000005$ ) nearly 100 times. M. O. F.

**Organic Syntheses by means of Ferric Chloride.** By MARCELLUS NENCKI (*Ber.*, 1899, 32, 2414—2419. Compare *Abstr.*, 1897, i, 520).—From the behaviour of a mixture of benzene and benzoic chloride towards ferric chloride, it is found that syntheses by means of this agent are to be explained on the same principle as those effected by the agency of aluminium chloride. The compound,  $(\text{COPh}_2, \text{FeCl}_3)_2, \text{COPhCl}, \text{FeCl}_3$ , prepared by adding sublimed ferric chloride to a mixture of benzene and benzoic chloride, forms yellowish-brown, hygroscopic crystals readily soluble in alcohol or ether, but insoluble in petroleum; water eliminates ferric chloride, and gives rise to benzophenone and benzoic acid (compare Morrell and Crofts, *Trans.*, 1898, 73, 347).

*Diacetylphloroglucinol*,  $\text{C}_6\text{HAc}_2(\text{OH})_3$ , prepared by heating phloroglucinol with acetic chloride and ferric chloride on the water-bath, and hydrolysing the ether thus produced, crystallises from water in pale yellow needles; it combines with 2 mols. of phenylhydrazine and hydroxylamine, forming pyrazoline and isoxazole derivatives respectively.

Syntheses by means of ferric chloride are sometimes attended by oxidising action. Chloroform and benzene, for instance, give rise to triphenylcarbinol, together with triphenylmethane, whilst acetic

chloride and metaxylene yield orthoparaxylic acid along with dimethylacetophenone; dibutylquinone is obtained instead of dibutylquinol from butyl chloride and quinol. M. O. F.

**Syntheses of Organic Compounds by means of Ferric Chloride.** By N. MEISSEL (*Ber.*, 1899, 32, 2419—2423. Compare foregoing abstract, and *Abstr.*, 1897, i, 521).—Syntheses of dimethylacetophenone, dimethylbenzophenone, cymeneacetophenone, and tertiary butylmethylacetophenone have been effected by the agency of ferric chloride; the last named ketone, prepared from tertiary parabutyltoluene and acetic chloride, boils at 240—245°, and has a sp. gr. 0.9541 at 15°.

Triphenylmethane, triphenylcarbinol, and a small quantity of benzaldehyde are obtained by the action of ferric chloride on chloroform and benzene. Para-isoamylphenol,  $C_5H_{11} \cdot C_6H_4 \cdot OH$ , prepared from isoamylic chlorocarbonate, phenol, and ferric chloride, was obtained by Liebmann on heating phenol with isoamylic alcohol and zinc chloride at 180°; it crystallises from petroleum, and melts at 93—94°. Parethylphenol is formed in the same way. M. O. F.

**Action of Tertiary Butylic Chloride on Dihydric Phenols in presence of Ferric Chloride.** By A. GUREWITSCH (*Ber.*, 1899, 32, 2424—2428. Compare the foregoing abstracts).—*Dibutylresorcinol*,  $C_6H_2Bu_2(OH)_2$ , crystallises in small plates containing  $2H_2O$ , and melts at 116—118°; the *diacetyl* derivative melts at 138°. The *butylic ether* of dibutylresorcinol, prepared by heating resorcinol with tertiary butylic chloride and ferric chloride, crystallises from dilute alcohol in white scales, and melts at 99°; aluminium chloride differs from ferric chloride in giving rise to dibutylresorcinol instead of the butylic ether. A mixture of concentrated nitric and sulphuric acids converts dibutylresorcinol into trinitroresorcinol, which melts at 175.5°.

*Diamylresorcinol*,  $C_6H_2(C_5H_{11})_2(OH)_2$ , obtained from resorcinol, tertiary amylic chloride, and ferric chloride, crystallises from dilute alcohol in needles and melts at 67°; the *diacetyl* derivative melts at 87—88°.

*Dibutylcatechol*,  $C_6H_2Bu_2(OH)_2$ , prepared from catechol, tertiary butylic chloride, and ferric chloride, crystallises from benzene in golden-yellow needles and melts at 85—86°.

*Dibutylquinone*,  $C_6H_2Bu_2O_2$ , produced on agitating quinol, tertiary butylic chloride and ferric chloride during 10 minutes at ordinary temperatures and pouring the liquid into water, crystallises from dilute alcohol, and melts at 150—151°; the *phenylhydrazone* crystallises from benzene and melts at 212°.

Butylphenol and para-amylphenol have been prepared by similar methods. M. O. F.

**Tertiary Dibutylpyrogallol.** By L. RÓŻYCKI (*Ber.*, 1899, 32, 2428—2429. Compare foregoing abstracts).—*Dibutylpyrogallol*,  $C_6H_2Bu_2(OH)_3$ , prepared by heating pyrogallol with tertiary butylic chloride and ferric chloride, crystallises from petroleum in snow-white needles and melts at 119°; the *triacetyl* derivative melts at 163°.

M. O. F.

**Retardation of Chemical Reactions due to Stereochemical Causes.** By MAX SCHOLTZ (*Ber.*, 1899, 32, 2251—2256).—It has been previously shown (*Abstr.*, 1898, i, 305, 383, 565; and this vol., i, 541) that pentacyclic compounds are formed by the action of  $\alpha\delta$ -dibromides on primary aromatic amines, unless other groups are in ortho-positions relatively to the amido-group, and that in such cases derivatives of  $\alpha\delta$ -diamido-compounds are formed. The research has been extended by studying the action of trimethylenic bromide on aromatic amines, and somewhat similar results have been obtained, although there is not the same tendency to form a tetracyclic nitrogen system as there is to form a pentacyclic compound. Diphenyltrimethylenediamine, N-phenyltrimethyleneimine, and diphenylbistrimethylenedi-imine are all formed by the action of trimethylenic bromide on aniline. Diphenyltrimethylenediamine is a yellow, viscid liquid, and distils at 280—285° under 16 mm. pressure (compare Hanssen, *Abstr.*, 1877, 577); it combines with either one or two equivalents of acid. The sulphate,  $C_{15}H_{18}N_2 \cdot H_2SO_4$ , melting at 156°, *hydrochloride* melting at 145°, and *platinochloride* have all been prepared.

N-phenyltrimethyleneimine,  $CH_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{NPh}$ , obtained by repeated fractional distillation of the first fractions from the diamine, is a colourless, limpid oil distilling at 130—132° under 16 mm., and at 242—245° under atmospheric pressure. Its *picrate*,  $C_9H_{11}N \cdot C_6H_3N_3O_7$ , crystallises in needles, and is readily soluble in alcohol. The third product, which is contained in the higher fractions, has not been obtained in a pure form.

Diorthotolyltrimethylenediamine,  $CH_2(CH_2 \cdot NH \cdot C_6H_4Me)_2$ , is the only condensation product obtained by heating an alcoholic solution of orthotoluidine (4 mols.) and trimethylenic bromide (1 mol.) for several hours on the water-bath; it is separated from orthotoluidine hydrobromide by extraction with ether, and forms a yellowish oil distilling at 275—280° under 16 mm. pressure; its *sulphate* melts at 216°.

Diphenylhexahydropyrimidine,  $CH_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{NPh} \\ \text{CH}_2 \cdot \text{NPh} \end{smallmatrix} CH_2$ , is obtained as a crystalline deposit when diphenyltrimethylenediamine is well shaken with 40 per cent. formaldehyde solution at 40—50°; it crystallises from alcohol in colourless prisms melting at 87°. Neither diorthotolyltrimethylenediamine nor the corresponding para-compound (Bischoff, this vol., i, 280) is capable of undergoing condensation with formaldehyde. A toluene solution of diparatolyltrimethylenediamine reacts with a solution of carbonyl chloride in the same solvent, yielding the *chloride*,  $CH_2[CH_2 \cdot N(COCl) \cdot C_6H_4Me]_2$ , which crystallises in colourless prisms melting at 82°.

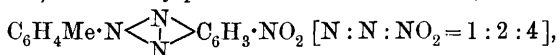
J. J. S.

**Action of Acid Chlorides on Benzyldeneaniline.** By KARL GARZAROLLI-THURNLACKH (*Ber.*, 1899, 32, 2277—2279).—Molecular proportions of acetic or benzoic chloride react with benzyldeneaniline at the ordinary temperature to form yellow, crystalline additive products of the formula  $COR \cdot NPh \cdot CHPhCl$ , which are difficult to purify and easily decomposed. The constitution is deduced from the fact that on boiling with alcohol they are decomposed into benzaldehyde,

hydrogen chloride and acetanilide or phenylbenzamide, according to the acid chloride used. J. F. T.

**Resolution of Isodiphenylhydroxyethylamine into its Optically Active Components.** By EMIL ERLÉNMEYER, jun. (*Ber.*, 1899, 32, 2377—2378).—On adding *d*-tartaric acid to a solution of isodiphenylhydroxyethylamine (this vol., i, 760) in absolute alcohol, the *tartrate* of the *lævo*-modification of the base separates nearly quantitatively in long needles; it melts at 176—177°, and in aqueous solution has  $[\alpha]_D - 37.57^\circ$ , whilst the *base* melts at 113—114°, and has  $[\alpha]_D - 109.66^\circ$  in alcoholic solution. The *tartrate* of the *dextro*-modification is very soluble in alcohol, melts at 133—134°, and in aqueous solution has  $[\alpha]_D + 54.33^\circ$ ; the *dextro*-*base* melts at 112—113°, and has a specific rotatory power equal in magnitude to that of the *lævo*-modification. W. A. D.

**Paratolylpseudoazimidonitrobenzene, Picryl, and 2:4-Dinitrophenylmetaxylylhydrazine, and their Derivatives.** By CONRAD WILLGERODT and HERMANN KLEIN (*J. pr. Chem.*, 1899, [ii], 60, 97—112).—Paratolylpseudoazimidonitrobenzene,



is best prepared by the action of sodium hydrogen carbonate on an alcoholic solution of tolylhydrazine and  $\alpha$ -chlorodinitrobenzene. When reduced with stannous chloride, it gives the corresponding *amine*, which melts at 212—213° and crystallises from alcohol in yellow flakes, but on one occasion separated in pale green, silky needles having the same melting point; it dissolves slightly in ethylic alcohol with a bluish-green fluorescence, more readily in methylic alcohol, and very slightly in boiling water with a green fluorescence, slightly in ether with a blue fluorescence, slightly in cold but readily in hot chloroform with a reddish fluorescence, readily in acetone with a blue fluorescence, slightly in benzene with a reddish-violet fluorescence, very slightly in boiling light petroleum or carbon bisulphide, and very readily in boiling acetic acid, but without fluorescence; the solutions are all yellow except those in benzene, light petroleum, and water; the fluorescence disappears on adding acids. The *hydrochloride* is a grey, crystalline powder, and the *platinochloride*, *sulphate*, and *nitrate* are also described. *Paratolylpseudoazimidobenzene*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_3\cdot\text{C}_6\text{H}_4$ , prepared by the action of nitrous acid on the base, melts at 114°, is insoluble in water, but slightly soluble in acetic acid and in alcohol, from which it crystallises in long, white, glistening needles; it is readily soluble in acetone, and very readily in ether, chloroform, or benzene.

*Metaxylylhydrazine*  $[\text{Me}:\text{Me}:\text{N}_2\text{H}_3 = 1:3:4]$  (Klauber, *Abstr.*, 1891, 1362) is best prepared by reducing the diazochloride with stannous chloride, and is obtained in white, crystalline flakes, but becomes brown and oily when exposed to air and light. *Picrylmetaxylylhydrazine*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , prepared by the action of picryl chloride on the hydrazine, melts at 160°, crystallises from alcohol in slender, yellow needles, and dissolves in most organic solvents.

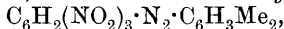
*Metaxylylaznitrosodinitrobenzene*,  $C_6H_3Me_2 \cdot N \begin{smallmatrix} \diagup N \\ \diagdown NO \end{smallmatrix} C_6H_2(NO_2)_2$ , is

prepared by boiling the hydrazine with acetic acid, from which it crystallises in beautiful, glistening, golden-yellow flakes; it melts at  $192^\circ$ , and is insoluble in water, but dissolves readily in organic solvents; its constitution is shown by the fact that it does not give the nitroso-reaction, is reduced by heating with alcohol or hydriodic acid to the pseudoazimido-compound, and is oxidised to an oxaznitroso-compound,  $-N \begin{smallmatrix} \diagup O \\ \diagdown NO \end{smallmatrix} N-$ , and not to the original nitro-compound.

*Metaxylylpseudoazimidodinitrobenzene*,  $C_6H_3Me_2 \cdot N_3 \cdot C_6H_2(NO_2)_2$ , crystallises in glistening, yellow needles, melts at  $125^\circ$ , and is insoluble in water, but more or less soluble in organic solvents. By the action of potassium iodide and acetic acid on metaxylylaznitrosodinitrobenzene there is produced a compound,  $C_{14}H_{11}O_3N_5$ , to which the structure  $C_6H_3Me_2 \cdot N_3 \cdot C_6H_2(NO) \cdot NO_2$ , or

$NO_2 \cdot C_6H_2 \begin{smallmatrix} \diagup N \\ \diagdown NO \end{smallmatrix} N \cdot C_6H_3Me_2$ , is assigned; it melts at  $116^\circ$ , is

insoluble in water, but soluble in organic solvents, and crystallises from alcohol in slender, brown needles. *Picrylazometaxylylene*,



prepared by oxidising the corresponding hydrazine with chromic acid at the ordinary temperature, melts at  $215-216^\circ$ , crystallises in beautiful, reddish, glistening flakes, and is insoluble in water, but soluble in organic solvents.

*2:4-Dinitrophenylmetaxylylhydrazine*,  $C_6H_3Me_2 \cdot NH \cdot NH \cdot C_6H_3(NO_2)_2$ , prepared by the action of  $\alpha$ -chlorodinitrobenzene on 1:3:4-metaxylylhydrazine, crystallises from alcohol in yellow, glistening needles, decomposes at  $179^\circ$ , and is insoluble in water, but soluble in organic

solvents. *Metaxylylaznitrosonitrobenzene*,  $C_6H_3Me \cdot N \begin{smallmatrix} \diagup N \\ \diagdown NO \end{smallmatrix} C_6H_3 \cdot NO_2$ ,

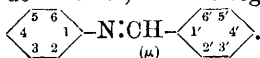
crystallises from acetic acid in yellow plates and decomposes at  $158^\circ$ .

*Metaxylylpseudoazimidonitrobenzene*,  $C_6H_3Me_2 \cdot N_3 \cdot C_6H_3 \cdot NO_2$ , melts at  $138^\circ$ , crystallises from alcohol in brownish-yellow needles, is insoluble in water, slightly soluble in ether, and readily in acetic acid, chloroform, benzene, or acetone.

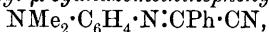
*2:4-Dinitrophenylazometaxylylene*,  $C_6H_3(NO_2)_2 \cdot N_2 \cdot C_6H_3Me_2$ , crystallises from acetic acid in slender, glistening, red needles, melts at  $204^\circ$ , is insoluble in water, slightly soluble in ether, and readily in acetic acid, chloroform, benzene, or acetone.

T. M. L.

**Condensation of Aromatic Nitroso-compounds with Methylene-Derivatives.** By PAUL EHRLICH and FRANZ SACHS (*Ber.*, 1899, 32, 2341—2346).—Aromatic nitroso-compounds condense with methylene derivatives in presence of more or less alkali, to form compounds of the type  $R \cdot N : CR^1R^2$ . The compounds described in this paper are prepared by the action of nitroso-compounds on benzylic cyanide and its derivatives, and are regarded as derived from phenylazimethinephenyl,

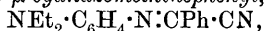


4-Dimethylamidophenyl- $\mu$ -cyanazomethinephenyl,



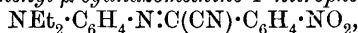
prepared by the action of caustic soda on a boiling alcoholic solution of nitrosodimethylaniline and benzylic cyanide, melts at  $90^\circ$ , crystallises from alcohol in long, orange-red needles with a bluish shimmer, dissolves only slightly in most solvents in the cold, and is insoluble in water. By the further action of alkali, a colourless *base* is produced, which has the composition  $\text{C}_{14}\text{H}_{14}\text{ON}_2$ , melts at  $228^\circ$ , dissolves very slightly in cold toluene, and forms a *hydrochloride* which melts at  $238^\circ$ . By boiling with dilute sulphuric acid, the condensation product was hydrolysed to benzoic cyanide (m. p.  $32^\circ$ ) and dimethylphenylenediamine, which was identified by the coloration with chromic acid, and by the methylene-blue reaction. A reduction product could not be isolated; zinc-dust and acetic acid gave dimethylphenylenediamine with hydrogen cyanide and benzaldehyde, whilst zinc-dust with calcium chloride and ammonium chloride in alcoholic solution gave dimethylphenylenediamine, ethylic phenylacetate, and other products.

4-Diethylamidophenyl- $\mu$ -cyanazomethinephenyl,



melts at  $112^\circ$ , crystallises from alcohol in splendid, scarlet-golden, glistening needles, and from ethylic acetate in large, well-formed, garnet-like crystals, with a greenish-golden reflection, dissolves most readily in chloroform, fairly readily in hot alcohol, methylic alcohol, acetone, methylal, carbon bisulphide, or ether, less readily in light petroleum, and not at all in water. By shaking with hydrochloric acid, the compound is decolorised, and benzoic chloride is produced. By boiling with alcoholic potash, a *substance* is produced which separates from alcohol in colourless crystals, melts at  $172^\circ$ , and dissolves readily in acids.

4-Diethylamidophenyl- $\mu$ -cyanazomethine-4'-nitrophenyl,



is produced by merely mixing nitrosodiethylaniline and paranitrobenzylic cyanide in alcoholic solution, whilst a single drop of alkali, ammonia, or an amine causes an extremely vigorous reaction; it melts at  $152^\circ$ , crystallises from alcohol in steel-blue, glistening needles with a greenish reflection, which are quite opaque and only show a violet-red colour in very thin layers; the solutions are cherry-red, and the vapour of the substance, which is volatile without decomposition, is of an intense brownish-yellow colour; it dissolves fairly readily in chloroform, less readily in hot alcohol, acetic acid, ethylic acetate, light petroleum, or benzene, but only slightly in these solvents in the cold, or in ether. It dyes wool and silk directly in dilute alcoholic or acetic acid solution, giving violet-red shades. The corresponding compound from nitrosodimethylaniline sinters at  $168^\circ$  and melts at  $176^\circ$ , whilst that from paranitrosomethylaniline separates from alcohol in brownish-violet, glistening crystals and melts at  $186^\circ$ .

T. M. L.

**Action of Phenylhydrazine on Tricarballic and Citric Acids.** By C. MANUELLI and E. DE RIGHI (*Gazzetta*, 1899, 29, ii, 148—161).—*Tricarballdiphenylhydrazide*, obtained by the action of

two mols. of phenylhydrazine on one of tricarballic acid, or by boiling an alcoholic solution of phenylhydrazine tricarballicylate, has the constitution  $N_2HPh \begin{smallmatrix} \diagup CO \cdot CH_2 \\ \diagdown CO \cdot CH \cdot CH_2 \cdot CO \cdot N_2H_2Ph \end{smallmatrix}$ . It crystallises from dilute acetic acid solution in microscopic, white needles melting at  $229-230^\circ$ ; it is almost insoluble in benzene, alcohol, chloroform, or ethylic acetate, but dissolves in hot glacial acetic acid; it is reduced by zinc dust with the formation of pyrroline. The *dibenzoyl* derivative,  $C_{32}H_{26}O_5N_4$ , forms an amorphous powder, which softens at  $137^\circ$  and melts at  $140-145^\circ$ . The *dinitroso*-derivative forms microscopic, yellowish-brown crystals.

*Phenylhydrazine tricarballicylate*,  $C_{18}H_{24}O_6N_4$ , crystallises in minute plates melting at  $180^\circ$ , and is very soluble in water or alcohol, but only slightly so in benzene or ether.

*Citryldiphenylhydrazide*,  $N_2HPh \begin{smallmatrix} \diagup CO \cdot CH_2 \\ \diagdown CO \cdot C(OH) \cdot CH_2 \cdot CO \cdot N_2H_2Ph \end{smallmatrix}$ ,

obtained either from citric acid and phenylhydrazine or by heating phenylhydrazine citrate, separates from ethylic acetate in small, sparkling, white crystals melting at  $208^\circ$ ; it crystallises well from orthonitrotoluene, and dissolves in glacial acetic acid with partial decomposition. The *diacetyl* derivative forms a yellowish-white, crystalline powder melting at  $138^\circ$ . The *dibenzoyl* derivative is obtained as an almost white, amorphous powder which melts at  $129-130^\circ$ , and is very soluble in all organic solvents. The *dibenzoyl-mononitroso*-derivative,  $C_{32}H_{25}O_7N_5$ , is a yellowish powder very soluble in organic solvents, and when purified by precipitating its benzene solution by means of light petroleum, melts and decomposes at  $83-88^\circ$ ; with phenol and sulphuric acid, it gives Liebermann's reaction. The *nitroso*-derivative is an unstable, yellowish-red substance.

*Acetylcitric acid triphenylhydrazide*,  $C_{26}H_{28}O_5N_6$ , prepared by the action of phenylhydrazine on an ethereal solution of acetylcitric anhydride, separates from alcohol in white crystals melting at  $138^\circ$ . It is readily soluble in glacial acetic acid, slightly so in chloroform or alcohol, and is insoluble in ether, benzene, light petroleum, or ethylic acetate; it is decomposed on heating with dilute alkalis or mineral acids. Its *triacetyl* derivative,  $C_{32}H_{34}O_8N_6$ , which is deposited from alcoholic solution in small, white crystals melting at  $132^\circ$ , is slightly soluble in benzene, more so in alcohol or ethylic acetate, but is insoluble in light petroleum.

*Phenylhydrazine citrate*,  $C_{18}H_{26}O_8N_4 + H_2O$ , crystallises from dilute alcohol in small, white plates melting at  $102^\circ$ . On heating with concentrated sulphuric acid, it gives a good yield of paraphenylhydrazine-sulphonic acid.

T. H. P.

**Diphenylcarbamide-oxime.** By ROBERT STOLLÉ (*Ber.*, 1899, 32, 2238).—By heating with alcoholic hydroxylamine, thiocarbanilide is converted into *diphenylcarbamide-oxime*,  $C_{13}H_{13}ON_3$ , which melts at  $151^\circ$ , is soluble in acids and alkalis, and reduces ammoniacal silver oxide.

A. H.

**Three Crystalline Forms of Dimetanitrodiphenylcarbamide.** By A. OFFRET and HENRI VITTENET (*Bull. Soc. Chim.*, 1899, [iii], 21, 788—797).—Further study of the crystalline forms assumed by dimetanitrodiphenylcarbamide has revealed the existence of a third isomeric modification in addition to the two which have already been shortly described (this vol., i, 692). The  $\alpha$ - and  $\beta$ -modifications are best obtained by slowly evaporating, in a current of dry air, a solution in 95 per cent. alcohol of either of the three modifications, or of a mixture thereof. In this process, the temperature should be maintained nearly constant at some point between 30° and 75°, the higher temperature being most favourable to the production of the yellow crystals of the  $\alpha$ -modification, whilst at lower temperatures the  $\beta$ -modification, which crystallises in white needles, is formed in larger proportion. The third, or  $\gamma$ -modification, crystallises in yellow plates, and is obtained by the spontaneous evaporation at the ordinary temperature of the alcoholic mother liquors, from which the other two modifications have been separated. The formation of the three modifications depends entirely on the conditions under which crystallisation takes place, and any one of the three forms may, by suitable regulation of the temperature, be converted into the other two. In the presence of alcohol, the  $\gamma$ -modification is stable at the ordinary temperature, but entirely disappears at about 40°, its place being taken first by the  $\beta$ -modification, which is most stable at about 50°, and then by the  $\alpha$ -modification, which is the most stable of the three forms. When heated in the dry state, the  $\alpha$ -modification remains unaltered until it melts at 242°; the crystals of the  $\beta$ -modification become yellow and opaque at 180°, and finally melt at 242°; and the yellow crystals of the  $\gamma$ -modification become white and opaque at 60°, finally melting at 242°. If anhydrous acetic acid, or a mixture of alcohol and acetic acid, is used as the solvent, the white needles of the  $\beta$ -modification only are obtained on cooling the solution. This action of acids explains the fact that dimetanitrodiphenylcarbamide is obtained in the form of a *white* powder by the action of carbonyl chloride on metanitriline, whereas when phenylic carbonate is employed a *yellow* product is formed.

A detailed account of the crystallographic and optical properties of the three modifications is given in the paper; each crystallises in the monoclinic system, but the three forms are quite distinct. N. L.

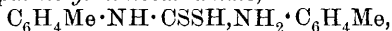
**Preparation of Aromatic Thiocarbamides.** By A. HUGERSHOFF (*Ber.*, 1899, 32, 2245—2249).—The reaction between aromatic amines and carbon bisulphide in presence of alcohol is greatly hastened by the presence of free sulphur. Under these conditions, aniline, ortho- and para-toluidine, paraphenetidine, paramidophenol,  $\alpha$ - and  $\beta$ -naphthylamine, and parabromaniline can all be quantitatively converted into the corresponding thiocarbamides in 1—2 hours. Pure carbon bisulphide undergoes the reaction much less readily than that which has been exposed to light, and contains free sulphur, and the reaction also takes place more slowly when the mixture is heated in the dark than when the preparation is carried out in the light. Hydrogen sulphide alone does not accelerate the reaction in the same



way as free sulphur, but the exact part played by the latter has not yet been ascertained.

In some cases, a thiocarbamate is first formed when sulphur is added to the mixture of the amine with carbon bisulphide, and this then decomposes.

*Paratoluidine paratolylldithiocarbamate,*



forms soft, crystalline scales, which melt and decompose at  $54^\circ$ . On exposure to the air, it slowly decomposes, hydrogen sulphide being evolved, sulphur liberated, and paratolylthiocarbamide produced.

A. H.

**Transformation of Alkylidithiocarbamates,  $\text{NHR}\cdot\text{CS}\cdot\text{SR}'$ , into Alkylidimidodithiocarbonates,  $\text{NR}'\cdot\text{C}(\text{SR}')_2$ .** By EMIL FROMM and M. BLOCH (*Ber.*, 1899, 32, 2212—2214).—It has been already shown that, whereas the groups  $-\text{NH}\cdot\text{CO}\cdot\text{OR}$  and  $-\text{NH}\cdot\text{CO}\cdot\text{SR}$  do not react in a tautomeric form, the group  $-\text{NH}\cdot\text{CS}\cdot\text{SR}$  in benzylic trithioimidocarboxylate does react in the tautomeric form  $-\text{N}:\text{C}(\text{SH})\cdot\text{SR}$  (*Abstr.*, 1895, i, 605); it is now shown that the same group in a dithiocarbamate or urethane reacts in a similar manner. *Benzylic phenyldithiocarbamate*,  $\text{NHPh}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ , is formed when phenylcarbimide and benzylic hydrosulphide are heated together for 7 hours at  $140^\circ$ ; it melts at  $84\text{--}85^\circ$ ; when treated with aqueous sodium hydroxide and benzylic chloride in equivalent proportions, it yields *dibenzylic dithiophenylimidocarbonate*,  $\text{NPh}:\text{C}(\text{S}\cdot\text{CH}_2\text{Ph})_2$ ; this melts at  $64\text{--}65^\circ$ , and, when boiled with concentrated hydrochloric acid, yields aniline (and not benzylaniline, as the formula  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{CS}\cdot\text{SCH}_2\text{Ph}$  would require) amongst the products of hydrolysis.

C. F. B.

**Action of Organic Bases on Urethane.** By C. MANUELLI and E. RICCA-ROSELLINI (*Gazzetta*, 1899, 29, ii, 124—136).—Urethane reacts with metabromaniline, ortho-, meta-, and para-chloraniline, meta- and para-nitraniline, paratoluidine, nitrotoluidine [ $\text{Me}:\text{NO}_2:\text{NH}_2 = 1:2:4$ ], 1:3:4-xylydine and normal heptylamine, giving rise to the corresponding symmetrical dialkylcarbamides, thus:  $\text{NH}_2\cdot\text{COOEt} + 2\text{NH}_2\text{R} = \text{CO}(\text{NHR})_2 + \text{NH}_3 + \text{EtOH}$ .

With orthonitraniline, urethane does not react, the only product besides unaltered nitraniline being cyanuric acid formed by condensation of the urethane; nitrotoluidine also [ $\text{Me}:\text{NH}_2:\text{NO}_2 = 1:3:4$ ] has no action on urethane.

*Diheptylcarbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_7\text{H}_{15})_2$ , which separates from alcohol in small, white, flattened needles melting at  $91^\circ$ , is soluble in benzene, but insoluble in water.

T. H. P.

**Action of Primary Amines on Urethanes.** By C. MANUELLI and E. COMANDUCCI (*Gazzetta*, 1899, 29, ii, 136—148).—Primary amines react with phenylurethane, giving the corresponding  $\alpha\beta$ -substituted carbamides thus:  $\text{NHPh}\cdot\text{COOEt} + \text{NH}_2\text{R} = \text{NHPh}\cdot\text{CO}\cdot\text{NH}_2\text{R} + \text{EtOH}$ . Allylurethane, however, with aniline, gives symmetrical diphenylcarbamide, and with heptylamine, symmetrical diheptylcarbamide.

Phenylurethane and parachloraniline react together, forming  $\alpha$ -phenyl- $\beta$ -parachlorophenylcarbamide.

*α-Phenyl-β-metabromophenylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$ , prepared from phenylurethane and metabromaniline, crystallises from alcohol in slender, white needles melting at  $235-236^\circ$ , and is almost insoluble in ether, water, or benzene.

*α-Phenyl-β-orthonitrophenylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , crystallises from water or alcohol in long needles of a pale maroon colour melting at  $231-233^\circ$ .

Phenylurethane and metanitrilaniline give *α-phenyl-β-metanitrophenylcarbamide*.

*α-Phenyl-β-paratolylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$ , prepared from phenylurethane and paratoluidine, separates from alcohol in very long, glistening, white crystals melting at  $259-260^\circ$ , and is soluble in benzene or ethylic acetate, but only slightly so in ether.

*α-Phenyl-β-metaxylylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me}_2[\text{Me}:\text{Me}:\text{NH} = 1:3:4]$ , is deposited from alcoholic solution in minute, glistening, white, acicular crystals melting at  $242-243^\circ$ ; it is soluble in benzene or acetic acid, but only very slightly so in ether or water.

*α-Phenyl-β-α-naphthylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$ , crystallises from alcohol in slender, white, silky needles which blacken at about  $274^\circ$  and melt at  $277-278^\circ$ ; it is slightly soluble in water or chloroform, more so in benzene.

Phenylurethane and piperidine react, forming *α-phenyl-β-piperidylcarbamide*.

*α-Phenyl-β-amylcarbamide*,  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_5\text{H}_{11}$ , which separates from dilute alcohol in slender, white prisms melting at  $238^\circ$ , is slightly soluble in ether, benzene, or acetic acid, and to a greater extent in ethylic acetate.

*Allylurethane*,  $\text{C}_3\text{H}_5 \cdot \text{NH} \cdot \text{COOEt}$ , obtained by the action of ethylic chlorocarbonate on allylamine, is a colourless liquid having a density 1.004 and boiling at  $194.5^\circ$  under 757.27 mm. pressure. T. H. P.

**Resolution of Racemic Amido-acids into Optically Active Components.** By EMIL FISCHER (*Ber.*, 1899, 32, 2451—2471).—Previous attempts to resolve synthetical amido-acids into optically active components have been confined to fractional crystallisation and selective fermentation. The compounds in question are usually so feebly acidic and basic that their salts with alkaloids or with optically active acids do not lend themselves to resolution by crystallisation. The author has therefore increased the acidity of amidopropionic, aspartic, and glutamic acids by introducing the benzoyl radicle, and then resolved the racemic benzoyl derivatives into their optically active components by crystallising certain alkaloidal salts; the active amido-acids are finally obtained by hydrolysing the benzoyl derivatives.

*l-Benzoylalanine*, prepared by fractionally crystallising the brucine salt of racemic benzoylalanine, crystallises from water in lustrous plates and melts at  $147-148^\circ$  ( $150-151^\circ$  corr.). It dissolves in 85 parts of water at  $20^\circ$ , and a 1 per cent. aqueous solution has  $[\alpha]_D - 3.3^\circ$  at  $20^\circ$ . A solution in aqueous caustic soda has  $[\alpha]_D - 37.3^\circ$ . The *silver* salt is crystalline, and dissolves with difficulty in hot water; it darkens slowly on prolonged exposure to light. *l-Alanine* crystallises from dilute alcohol in small, colourless prisms, and melts, evolving gas, at  $297^\circ$  (the racemic acid decomposes at  $293^\circ$ ); the acid is very slightly active,

an 8·8 per cent. aqueous solution giving  $\alpha_D - 0\cdot21^\circ$  in a 1-decimetre tube. The *hydrochloride* crystallises in colourless needles, and has  $[\alpha]_D - 9\cdot68^\circ$  in aqueous solution. *d-Benzoylalanine* melts at  $147\text{--}148^\circ$ , and has  $[\alpha]_D + 37\cdot13^\circ$  in aqueous potash; *d-alanine* forms a *hydrochloride* which has  $[\alpha]_D + 9\cdot55^\circ$ . A cultivation of *Aspergillus niger* in an aqueous solution of racemic alanine destroys about 10 per cent. of the dextrorotatory constituent; *Penicillium glaucum* does not flourish in a 2 per cent. solution of alanine.

*Benzoyl-l-aspartic acid* dissolves in 3—4 parts of hot water, and in 261 parts of water at  $20^\circ$ , crystallising in needles; it melts at  $180\text{--}181^\circ$  ( $184\text{--}185^\circ$  corr.), and has  $[\alpha]_D + 37\cdot4^\circ$  in a solution containing 2 mols. of caustic potash. *Racemic benzoylaspartic acid* crystallises from water in lustrous, colourless plates containing  $1\text{H}_2\text{O}$ , and melts at  $161\text{--}162^\circ$  ( $164\text{--}165^\circ$  corr.); the dried acid dissolves in 3—4 parts of hot water, and in 200 parts of water at  $20^\circ$ , but 664 parts of water at  $20^\circ$  are required to dissolve the crystallised acid. *r-Benzoylaspartic acid* may be resolved into its active components by crystallising the brucine salt. *Benzoyl-d-aspartic acid* melts at  $180\text{--}181^\circ$ , and has  $[\alpha]_D - 37\cdot6^\circ$  in a solution containing 2 mols. of caustic potash.

*Racemic benzoylglutamic acid* crystallises from hot water in colourless leaflets containing  $1\text{H}_2\text{O}$ , and melts at  $152\text{--}154^\circ$  ( $155\text{--}157^\circ$  corr.); the hydrated acid dissolves readily in alcohol, and is soluble in 124 parts of water at  $20^\circ$ . The *silver* salt crystallises in slender, colourless needles. When natural, optically active glutamic acid is treated with benzoic chloride in presence of aqueous sodium hydrogen carbonate, a portion of it becomes racemised. *Benzoyl-l-glutamic acid*, obtained by crystallising the strychnine salt of the racemic acid, melts at  $128\text{--}130^\circ$  ( $130\text{--}132^\circ$  corr.), dissolves in less than 2 parts of boiling water, and in 21 parts of water at  $20^\circ$ ; a 5 per cent. aqueous solution has  $[\alpha]_D + 13\cdot81^\circ$ , an alkaline solution, containing 2 mols. of caustic potash, having  $[\alpha]_D - 18\cdot7^\circ$ . *Benzoyl-d-glutamic acid* sinters at  $128^\circ$ , and becomes completely fused at  $137\text{--}139^\circ$ ; a 10 per cent. solution containing 2 mols. of caustic potash has  $[\alpha]_D + 17\cdot18^\circ$ . *d-Glutamic acid* from the benzoyl derivative has  $[\alpha]_D + 30\cdot85^\circ$ , whilst the natural acid from casein has  $[\alpha]_D + 30\cdot45^\circ$ .

Attempts to resolve hippuric acid into optically active components by crystallising the quinine and brucine salts were unsuccessful. Racemic benzoyltyrosine forms a brucine salt which yields an active benzoyltyrosine which melts at  $163\text{--}164^\circ$  ( $166\text{--}167^\circ$  corr.), and has  $[\alpha]_D + 18\cdot8^\circ$  in alkaline solution. M. O. F.

**Condensation Product from Isobutaldehyde and Benzaldehyde.** By MILAN JOSEF STRITAR (*Monatsh.*, 1899, 20, 617—633).—An attempt was made to prepare the aldol corresponding with the glycol obtained by Swoboda and Fosseck (*Abstr.*, 1891, 31) and Reik (*Abstr.*, 1898, i, 246) by the action of alcoholic potash on a mixture of isobutaldehyde (2 mols.) and benzaldehyde (1 mol.). It is now found that by the action of a saturated solution of potassium carbonate or of solid potassium hydroxide on this mixture a compound,  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , is formed. This crystallises from glacial acetic acid in small needles melting at  $94^\circ$ , but its constitution is not yet determined. Reducing

agents resolve it into its constituents, but do not effect its reduction. On oxidation in pyridine solution with potassium permanganate and sulphuric acid, it yields phenylhydroxypivalic acid (Fittig and Jayne, *Abstr.*, 1883, 471). The *phenylhydrazone*,  $C_{11}H_{14}O, N_2HPh$ , is a white, crystalline powder melting at  $117^\circ$ , and is probably the phenylhydrazone of the required glycol. R. H. P.

**Condensation of the Cyanhydrins of Benzaldehyde and Anisaldehyde.** By STEPHEN S. MINOVICI (*Ber.*, 1899, 32, 2206—2209).—When hydrogen chloride is passed into an ethereal solution of benzaldehyde cyanhydrin,  $C_8H_7ON$ , kept at the ordinary temperature by means of cold water, a yellow compound is eventually precipitated which melts at  $200$ — $203^\circ$  and has the composition  $C_{16}H_{12}ON_2$ . It has no acid properties, and forms a salt with strong hydrochloric acid; the salt, however, is decomposed at once by water. It is very stable, and attempts to decompose it into well-defined products were unsuccessful; a *monobromo*- and a *mononitro*-derivative were obtained, however; these melt at  $200^\circ$  and  $232^\circ$  respectively, and the latter is amorphous in appearance. This same product of condensation is formed when quinol or catechol is also present; in the presence of resorcinol, mandelamide results.

Anisaldehyde cyanhydrin,  $C_9H_9O_2N$ , under the same circumstances, reacts in a different manner, yielding a white compound,  $C_{17}H_{15}O_3N$ . The red *dibromo*-derivative of this melts and decomposes at  $155^\circ$ , and is converted by water or alcohol into a white substance which contains bromine and melts at  $115^\circ$ ; the *dinitro*-derivative melts at  $200^\circ$ . C. F. B.

**Derivatives of Paratolualdehyde.** By WENZEL HANZLIK and AL. BIANCHI (*Ber.*, 1899, 32, 2282—2287. Compare this vol., i, 597).—*Paratoluylideneacetone*,  $C_6H_4Me \cdot CH : CH \cdot COMe$ , is produced in nearly theoretical quantity by shaking paratolualdehyde, acetone, and water in a 10 per cent. solution of sodium hydroxide; it separates from light petroleum in quadratic plates, melts at  $34$ — $35^\circ$ , and boils at  $155$ — $156^\circ$  under 16 mm. or  $277$ — $278^\circ$  under 739.4 mm. pressure, as a colourless, pleasant-smelling oil which solidifies on cooling; it is readily soluble in alcohol, ether, or carbon bisulphide, and dissolves in concentrated sulphuric acid with a blood-red coloration; the *phenylhydrazone* forms yellow leaflets melting at  $138^\circ$ . The *dibromide*,  $C_6H_4Me \cdot CHBr \cdot CHBr \cdot COMe$ , separates from light petroleum in white, crystalline crusts and melts at  $84$ — $85^\circ$ .

*Paratoluylideneacetophenone*,  $C_6H_4Me \cdot CH : CH \cdot CPh$ , prepared in the same way from paratolualdehyde and acetophenone, separates from light petroleum in pale yellow needles melting at  $96.5^\circ$ , and dissolves in concentrated sulphuric acid with an orange coloration which, on dilution, becomes an intense yellow; the *dibromide* forms white needles and melts at  $159^\circ$ ; the *oxime* crystallises from alcohol in needles melting at  $91^\circ$ , and the *phenylhydrazone* from a mixture of ether and light petroleum in yellow needles melting at  $129$ — $130^\circ$ .

*Metanitroparatoluylideneacetone*,  $NO_2 \cdot C_6H_3Me \cdot CH : CH \cdot COMe$ , prepared from metanitroparatolualdehyde and acetone, separates from alcohol in yellow needles, melts at  $91^\circ$ , and is readily soluble in

alcohol, ether, carbon bisulphide, or chloroform; it is coloured red by concentrated sulphuric acid and forms an orange coloured solution showing a green fluorescence. The *dibromide* forms flat crystals melting at  $112-113^{\circ}$ , and the *phenylhydrazone* crystallises from alcohol in well-formed, red crystals melting at  $146-147^{\circ}$ .

*Metanitroparatoluylideneacetophenone*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}:\text{CH} \cdot \text{COPh}$ , prepared from metanitroparatolualdehyde and acetophenone, separates from alcohol in yellow leaflets, melts at  $142-143^{\circ}$ , and is coloured red by concentrated sulphuric acid, forming an orange-coloured solution; the *dibromide* crystallises from carbon bisulphide and melts at  $171-172^{\circ}$ , the *oxime* from alcohol in small, well-formed crystals melting at  $71-72^{\circ}$ , and the *phenylhydrazone* from alcohol in brick-red leaflets melting at  $119^{\circ}$ .

On treatment with sodium acetate and acetic anhydride at  $150^{\circ}$ , metanitroparatolualdehyde yields *metanitroparamethylcinnamic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}:\text{CH} \cdot \text{COOH}$ , which separates from dilute alcohol in long, slender needles and melts at  $170-171^{\circ}$ ; it is readily soluble in alcohol, hot water, or ether, and forms a white, insoluble *silver* salt; the *methylic* and *ethylic* salts crystallise from a mixture of ether and light petroleum, the former in long, white needles melting at  $108-109^{\circ}$ , and the latter in monoclinic leaflets melting at  $96-97^{\circ}$ .

The formation of metanitroparamethylcinnamic acid in this reaction is preceded by the production of *metanitroparatoluylidene diacetate*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}(\text{OAc})_2$ , since this substance separates on the addition of an equal weight of acetic anhydride to the nitro-aldehyde; it crystallises from a mixture of ether and light petroleum in monoclinic plates, melts at  $98-98.5^{\circ}$ , and on treatment with anhydrous sodium acetate and acetic anhydride yields the corresponding cinnamic acid. On treating paramethylcinnamic acid with a mixture of concentrated sulphuric acid and nitric acid, it is transformed into *4-methyl-3-dinitrostyrene*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}:\text{CH} \cdot \text{NO}_2$ , which forms short, yellow needles melting at  $117-118^{\circ}$ , and on oxidation with potassium permanganate yields nitroterephthalic acid, or with dilute nitric acid, metanitroparatoluic acid.

J. F. T.

**Preparation of Aromatic Aldehydes and the Artificial Preparation of Indigo Dyes.** By MICHAËL I. KONOWALOFF (*Chem. Centr.*, 1899, i, 1074—1075; from *J. Russ. Chem. Soc.*, 1899, 31, 54—56).—Mesitylaldehyde melts at  $9^{\circ}$  and boils at  $220-222^{\circ}$ . The aldehydes, prepared by the method previously described (*J. Russ. Chem. Soc.*, 1898, 30, 960), were nitrated. The nitro-group enters into the benzene ring in the ortho-position when the meta-position is occupied by organic radicles. All the orthonitro-compounds so prepared, when treated with acetone and alkali, yielded homologues of indigo. Dimethyl-, tetramethyl-, and dimethylditertiarybutyl-indigo were prepared.

E. W. W.

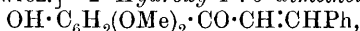
**Experiments on the Synthesis of Chrysin Derivatives.** By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1899, 32, 2260—2269).—In the hope of effecting a synthesis of chrysin, the method of Emilewicz and von Kostanecki (*Abstr.*, 1898, i, 369) for the synthesis of oxyflavones was applied to the phloroglucinol series;

it was found, however, that only coumaranone derivatives could be obtained from the condensation product of phloracetophenone dimethylic ether with benzaldehyde.

*Phloracetophenone trimethylic ether*,  $C_6H_2(OMe)_3 \cdot COMe$ , obtained by the action of acetic chloride on phloroglucinol trimethylic ether in the presence of sublimed ferric chloride, forms broad prisms, which, when recrystallised from dilute alcohol, melt at  $100^\circ$ ; on treatment with aluminium chloride at  $110^\circ$ , it is converted into *phloracetophenone dimethylic ether*,  $OH \cdot C_6H_2(OMe)_2 \cdot COMe$  [ $OH : (OMe)_2 = 2 : 4 : 6$ ], which separates from dilute alcohol in leaflets melting at  $82-83^\circ$ . The *acetyl* compound crystallises from alcohol in prisms and melts at  $107^\circ$ .

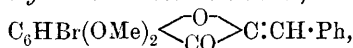
*Phloracetophenone triethylic ether*,  $C_6H_2(OEt)_3 \cdot COMe$ , prepared in the same way as the trimethylic ether, forms rhombic plates and melts at  $75^\circ$ ; with aluminium chloride, it yields the corresponding *diethylic ether*, which separates from dilute alcohol in needles melting at  $85^\circ$ .

[With T. EMILEWICZ.]—*2'-Hydroxy-4' : 6'-dimethoxychalkone*,



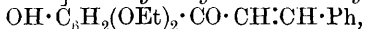
prepared by the action of phloracetophenone dimethylic ether on benzaldehyde in alcoholic sodium hydroxide solution, separates from alcohol in yellow, concentric needles melting at  $91-92^\circ$ , which are coloured orange by concentrated sulphuric acid, and give a yellow to light orange solution. The *sodium* derivative is deep yellow, and is dissociated by water. The *acetyl* derivative separates in leaflets melting at  $129-130^\circ$ , and on bromination passes into *2'-acetoxy-4' : 6'-dimethoxybromochalkone dibromide*,  $OAc \cdot C_6HBr(OMe)_2 \cdot CO \cdot CHBr \cdot CHPhBr$ , which crystallises in leaflets, and when rapidly heated melts at  $185^\circ$ , decomposing above this temperature with evolution of gas.

1 : 3-Dimethoxybenzylidenebromocoumaranone,



from the dibromide and alcoholic potassium hydroxide, separates from benzene in white needles melting at  $223^\circ$ , and dissolves in concentrated sulphuric acid with an orange coloration.

[With B. BEDNARSKI.]—*2'-Hydroxy-4' : 6'-diethoxychalkone*,

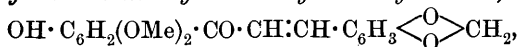


prepared from phloracetophenone diethylic ether and benzaldehyde, separates from alcohol in deep yellow, concentrically grouped needles, and melts at  $118-119^\circ$ ; concentrated sulphuric acid colours the crystals orange, and forms a yellow solution; the *acetyl* compound crystallises from dilute alcohol in yellow plates melting at  $25^\circ$ , and on bromination in carbon bisulphide solution gives *2'-acetoxy-4' : 6'-diethoxybromochalkone dibromide*,  $OAc \cdot C_6HBr(OEt)_2 \cdot CO \cdot CHBr \cdot CHPhBr$ , which forms leaflets melting and decomposing at  $169-170^\circ$ , and on treatment with alcoholic potassium hydroxide yields 1 : 3-diethoxybenzylidenebromocoumaranone,  $C_6HBr(OEt)_2 \begin{array}{c} \diagup O \diagdown \\ CO \end{array} C : CHPh$ , which separates from benzene in short, yellow needles melting at  $205^\circ$ , and behaves towards sulphuric acid similarly to the dimethoxy-derivatives.

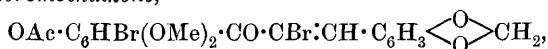
[With F. HERSTEIN.]—With the view of synthesising luteolin,

which according to A. G. Perkin is 1:3:3':4'-tetrahydroxyflavone, phloracetophenone dimethylic ether was condensed with piperonal, but as in the previous instance coumaranone derivatives alone were formed.

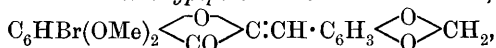
*2'-Hydroxy 4':6'-dimethoxy-3:4-methylenedioxychalkone,*



the first product of the condensation, separates from alcohol in clusters of slender needles and melts at 162—163°; with concentrated sulphuric acid, the crystals become coloured a fine red, the solution, however, quickly becoming opaque. The *acetyl* derivative separates from dilute alcohol in leaflets melting at 120—121°, and on bromination in chloroform solution gives *2'-acetoxy-4':6'-dimethoxy-3:4-methylenedioxydibromochalkone,*



which separates from a mixture of chloroform and alcohol in plates melting and decomposing at 168°. The constitution of this compound follows from the fact that, on treatment with alcoholic potash, it is converted into *1:3-dimethoxypiperonalbromocoumaranone,*



which separates from glacial acetic acid or a mixture of pyridine and alcohol as a crystalline precipitate, and melts at 274°, the solution in the latter solvent showing a marked green fluorescence. In concentrated sulphuric acid, it dissolves to a carmine red solution. J. F. T.

**Aromatic Nitro-compounds: Substitution of Nitro-groups by Methoxyl and Ethoxyl.** By W. REINDERS and W. E. RINGER (*Rec. Trav. Chim.*, 1899, 18, 326—329).—*Paramethoxybenzonitrile*, prepared by boiling a solution of paranitrobenzonitrile and sodium methoxide in methylic alcohol, and purified by distillation in steam and crystallisation from alcohol, separates in white needles, melts at 59°, and boils at 137·6° under 18·5 mm. pressure, and at 240·1° under ordinary pressure; its boiling points under intermediate pressures are also given. The substance is very soluble in the ordinary organic solvents, and is hydrolysed by caustic soda to paramethoxybenzoic acid.

*Parethoxybenzonitrile*, obtained by heating paranitrobenzonitrile with a dilute alcoholic solution of sodium ethoxide, crystallises in white needles and melts at 57°.

In the case of the methoxy-derivative, the yield is practically quantitative, but with the ethoxy-compound it is only 10 per cent. of that theoretically possible. G. T. M.

**Orthomethoxybenzonitrile and Orthethoxybenzonitrile.** By W. E. RINGER (*Rec. Trav. Chim.*, 1899, 18, 330—333).—*Orthomethoxybenzonitrile*, produced by heating a methylic alcoholic solution of orthonitrobenzonitrile with excess of sodium methoxide, is obtained as an oil, which, when cooled in a mixture of alcohol and solid carbonic anhydride, solidifies to a mass of crystals melting at 24·5°; it boils at 140° under 18 mm. pressure, and at 260° under ordinary pressure;

its boiling points under intermediate pressures are also recorded. The substance is not hydrolysed by boiling with 25 per cent. hydrochloric acid or 50 per cent. caustic potash, but when boiled with 50 per cent. sulphuric acid, it is converted into salicylic acid.

*Orthethoxybenzonitrile* melts at  $5^{\circ}$  and boils at  $153.5^{\circ}$  under 29 mm. and at  $263.5^{\circ}$  under 766 mm. pressure; other intermediate boiling points are also recorded. It is not attacked when boiled with 50 per cent. sulphuric acid, but a trace of salicylic acid is produced on boiling with acid of 70 per cent. G. T. M.

**Action of Iodine on Cinnamic Acid in Pyridine Solution.** By GIOVANNI ORTOLEVA (*Gazzetta*, 1899, 29, i, 503—509).—*Pyridine  $\beta$ -iodocinnamate*,  $C_{14}H_{12}O_2NI$ , obtained by the interaction in molecular proportion of a pyridine solution of cinnamic acid and an alcoholic solution of iodine, melts and decomposes at  $165$ — $166^{\circ}$ , is insoluble in alcohol, ether, or benzene, slightly soluble in boiling water, and dissolves slowly in alkalis with elimination of pyridine. It is soluble in dilute mineral acids, especially on heating, and separates unchanged in glistening, white scales. Treated with sodium hydroxide solution, it yields benzoylacetic acid and acetophenone.

*$\beta$ -Iodocinnamic acid*,  $C_9H_7I \cdot COOH$ , obtained by decomposing a sodium hydroxide solution of the pyridine salt with sulphurous acid, crystallises from benzene in white needles which melt at  $160$ — $162^{\circ}$  and in the air assume a yellowish coloration; it is only slightly soluble in water, but dissolves in alcohol or ether, and in sodium carbonate solution with effervescence. It decolorises potassium permanganate in the cold, and gives no coloration with ferric chloride. The calcium salt,  $(C_9H_6O_2I)_2Ca + 3\frac{1}{2}H_2O$ , crystallises in short, colourless needles, and the silver salt, in glistening, white scales, which on heating decompose with the formation of phenylacetylene, silver iodide, and carbonic anhydride. T. H. P.

**Monobromotruzone from  $\alpha$ -Bromallocinnamic Acid.** By W. MANTHEY (*Ber.*, 1899, 32, 2475—2476. Compare Abstr., 1882, 615, and 1898, i, 662).—Leuckart gave to the substance obtained by treating  $\alpha$ -bromallocinnamic acid with cold concentrated sulphuric acid the composition  $C_{17}H_{12}O_2Br_2$ ; in reality, it is a monobromotruzone, for on heating for 3 hours at  $180^{\circ}$  with hydriodic acid and red phosphorus, it is reduced to truxene, the latter being identified by oxidation to tribenzoylenebenzene (Abstr., 1878, 229; 1890, 514; 1898, i, 32).

On reducing monobromotruzone with zinc dust and acetic acid, Leuckart obtained a compound to which he ascribed the composition  $C_{17}H_{14}O_2$ ; his analytical results, however, approximate to those required for the formula for a dihydrotruxone,  $C_9H_8O$ . G. T. M.

**Preparation of Dibromindone from  $\alpha$ -Dibromocinnamic Acid.** By THEODOR LANSER (*Ber.*, 1899, 32, 2477—2478).—By adding bromine to phenylpropionic acid,  $\alpha\beta$ -dibromocinnamic and  $\alpha\beta$ -dibromoallicinnamic acids are produced; on treatment with concentrated sulphuric acid, the latter yields dibromindone, whilst the former remains unaltered; the current hypothesis of the stereochemical



relationship of these compounds furnishes a ready explanation of this result (compare Abstr., 1898, i, 662). In accordance with this view, it should be possible, either by distillation or other energetic treatment, to convert the dibromocinnamic acid,

$$\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{Br} \\ | \\ \text{Br} \cdot \text{C} \cdot \text{COOH} \end{array} \quad (\alpha\text{-acid, m. p.}$$

139°), into the dibromallocinnamic acid,

$$\begin{array}{c} \text{Ph} \cdot \text{C} \cdot \text{Br} \\ | \\ \text{COOH} \cdot \text{C} \cdot \text{Br} \end{array} \quad (\beta\text{-acid, m. p. } 100^\circ),$$

just as fumaric and allocinnamic acids are converted into their stereoisomerides. The  $\alpha$ -acid, which is not acted on by sulphuric acid, gives an 80 per cent. yield of dibromindone when distilled with phosphoric anhydride under 20 mm. pressure. Phenylpropionic acid hydrobromide, when similarly treated, yields monobromindone; this compound crystallises from dilute acetic acid in canary-yellow needles melting at 64—65°, is extremely soluble in all organic solvents, and decomposes spontaneously when left in the desiccator. G. T. M.

**Optical Resolution and Properties of Mandelic Acid.** By EBERHARD RIMBACH (*Ber.*, 1899, 32, 2385—2391. Compare Lewkowitsch, Abstr., 1883, 44, 1124).—A solution of mandelic acid and crystallised cinchonine in water is heated on the water-bath for an hour with constant shaking; the whole is allowed to remain overnight, and then separated from resinous matter by filtration; on adding crystals of cinchonine *d*-mandelate to the clear solution, kept at a temperature of 6—8°, a separation of the dextromandelate occurs. If strong brine is added to the mother liquor, a copious precipitate of cinchonine hydrochloride is produced, but this subsequently induces the gradual separation of a considerable quantity of cinchonine *d*-mandelate.

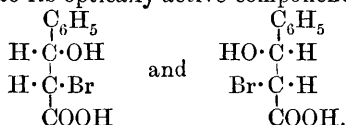
Dextromandelic acid melts at 133·8° and crystallises in hemimorphic, monoclinic crystals [ $a:b:c = 1.4180:1:2.9269$ ;  $\beta = 102^\circ 54' 43''$ ]; its specific rotatory power at 20° is  $[\alpha]_D + 215.51 - 0.5777q$ . The rotational dispersion is normal, but rather strong, the dispersion coefficient,  $[\alpha]_D$  blue/ $[\alpha]_D$  red, being, as a mean, 2.72. (Cane sugar, for an equal wave-length interval, has a coefficient of 2.33, and santonin of 2.96.) A mixture of dextromandelic acid with ordinary inactive mandelic acid in certain proportions has a melting point lower than that of either of its constituents; moreover, the solubility of inactive mandelic acid is increased by the addition of dextro-acid, and the solution becomes optically active. Inactive mandelic acid is therefore a racemic compound at the ordinary temperature, and no indication of a transition point has as yet been obtained.

*Cinchonine lævomandelate*, obtained from the mother liquor from the dextromandelate, had  $[\alpha]_D + 92.1$  at 20° in Hesse's liquid (1 volume of alcohol and 2 volumes of chloroform). It forms large, hemihedral, orthorhombic crystals [ $a:b:c = 0.7123:1:1.8252$ ]. Cinchonine dextromandelate has  $[\alpha]_D + 152.4$  at 20°, and could not be obtained in measurable crystals. The solubilities of both salts have been determined at several temperatures; at higher temperatures, the solubility curves approach one another, hence the necessity for the precaution of maintaining a low temperature in effecting the separation of the two compounds; lower temperatures than those above

recommended lead to impure separations, due, perhaps, to the formation of a partially racemic compound. A. L.

**Stereoisomeric Phenylbromolactic Acids.** By EMIL ERLÉNMEYER, jun., and A. MOEBES (*Ber.*, 1899, 32, 2375—2377).—The authors give details of the resolution of  $\alpha$ -bromophenyllactic acid into its optically active components by means of cinchonine (compare Abstr., 1891, 1482). The salt,  $C_{23}H_{31}O_4N_2Br$ , of the dextro-acid is less soluble in alcohol than that of the laevo-acid, and forms slender, white needles which decompose at 159—160°; the dextro-acid crystallises from chloroform in measurable crystals, melts at 119—120°, and has  $[\alpha]_D + 21.46$  in absolute alcohol. The laevo-acid could not be obtained pure; as isolated, it melted at 118—119°, and had  $[\alpha]_D - 15.55$ , showing that it was contaminated with the dextro-modification. Taking into account the preparation of  $\alpha$ -bromophenyllactic acid from cinnamic acid,  $\begin{matrix} H \cdot C \cdot Ph \\ | \\ H \cdot C \cdot COOH \end{matrix}$ ,

the authors assign to its optically active components the configurations



W. A. D.

**Synthesis of Parisopropylphenylhydroxypivalic Acid.** By L. SŠAPOŠCHNIKOFF (*Chem. Centr.*, 1899, i, 1204; from *J. Russ. Chem. Soc.*, 1899, 31, 250—254).—A 75 per cent. yield of crude *parisopropylphenylpivalic acid*,  $C_6H_4Pr \cdot CH(OH) \cdot CMe_2 \cdot COOH$ , is obtained by the action of the zinc-copper couple on ethylic bromisobutyrate and cuminol at 50°. The acid crystallises from water or aqueous alcohol in transparent needles, is only very slightly volatile in steam, melts at 106°, is very slightly soluble in cold water, and easily so in alcohol, ether, benzene, or glacial acetic acid. A determination of the molecular weight gave 224. The sodium salt crystallises with  $3H_2O$ , the barium and calcium salts with  $4H_2O$ , whilst the potassium and silver salts are anhydrous. All these salts are soluble in hot water, but sparingly so, or insoluble, in cold water. The copper, mercury, and lead salts are insoluble in cold water. By distilling the acid with a 25 per cent. solution of sulphuric acid, *parisopropylisobutenylbenzene*, boiling at 236—238° (compare Perkin, *Trans.*, 1879, 35, 141), is formed.

E. W. W.

**Ethylic Benzalanilacetoacetate [Anilinobenzylacetoacetate].** By CORRADO BERTINI (*Gazzetta*, 1899, 29, ii, 22—35).—*Dibenzalacetoneaniline* [*anilidobenzylbenzylideneacetone*],  $CHPh \cdot CH \cdot CO \cdot CH_2 \cdot CHPh \cdot NHPh$ , prepared by the interaction of dibenzylideneacetone and aniline in molecular proportion, separates from benzene in well-developed, lustrous yellow crystals melting at 129—130°. When warmed with dilute hydrochloric acid, it decomposes, with formation of benzaldehyde.

*Ethylic anilidobenzylacetoacetate oxime*,



prepared by the action of a sodium hydroxide solution of benzaldehyde

on a mixture of hydroxylamine hydrochloride, aniline, and ethylic acetoacetate, exists in two modifications. If the crude product of the reaction is rapidly heated with dilute alcohol so as to leave some undissolved, and the solution cooled, a white substance is obtained which melts at  $136\text{--}137^\circ$ , and is soluble in the ordinary solvents and in hot dilute hydrochloric acid, but insoluble in alkalis, and only slightly soluble in water. This form, which, if not very pure, reddens in the air, does not yield an acetyl derivative. If, however, the original product of the reaction is treated with cold alcohol, on filtering off the latter a white substance remains, which, when crystallised from boiling benzene, or precipitated from its solution in acetone by adding alcohol, forms a colourless, crystalline powder melting and decomposing at  $153^\circ$ ; it is insoluble in dilute sodium hydroxide solution or dilute hydrochloric acid, slightly soluble in benzene or light petroleum, and less soluble in alcohol than the other isomeride into which it is gradually converted on keeping. The oxime, melting at  $153^\circ$ , forms an *acetyl* derivative,  $\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}:\text{NOAc}$ , which crystallises from dilute alcohol in long, shining needles melting at  $114^\circ$ .

The *phenylhydrazone* also exists in two forms, probably the *syn*- and *anti*-modifications. One of them is a sandy, white, non-crystalline powder which, when purified by dissolving in chloroform and precipitating with light petroleum, melts and decomposes at  $79\text{--}80^\circ$ . It is insoluble in water, ether, or sodium hydroxide solution, but dissolves slightly in benzene or light petroleum, and more so in alcohol or chloroform; on heating with dilute hydrochloric acid, decomposition takes place with the separation of benzaldehyde. From the benzene-light petroleum mother liquors of this oxime, another form is slowly deposited which separates from alcohol in shining, white crystals melting at  $138\text{--}139^\circ$  with decomposition.

On heating ethylic anilidobenzylacetoacetate with a mixture of equal volumes of glacial acetic acid and alcohol, a *substance* is obtained which has the composition  $\text{C}_{16}\text{H}_{15}\text{ON}$ , and separates from benzene in large, well-developed crystals melting at  $155\text{--}156^\circ$ ; in benzene solution, it gives a molecular weight corresponding with the formula  $\text{C}_{32}\text{H}_{30}\text{O}_2\text{N}_2$ . It is a very stable, neutral compound, and is unchanged by boiling with alcoholic hydroxylamine or its hydrochloride; it dissolves in boiling acetic anhydride, but does not separate unaltered. When dissolved in carbon bisulphide, it takes up bromine with evolution of heat, and with iodine it forms a compound containing 42.6 per cent. of iodine.

A quantity of moist ethylic anilidobenzylacetoacetate, when kept in a closed vessel for about six months, changed spontaneously into the diethylic diphenyldihydrodicarbolutidinate obtained by Lachowicz by the prolonged action, at the ordinary temperature, of 2 mols. of aniline and 2 mols. of benzaldehyde on an alcoholic solution of 1 mol. of ethylic acetoacetate.

On the dry distillation of ethylic anilidobenzylacetoacetate, a considerable quantity of symmetrical diphenylcarbamide is formed.

T. H. P.

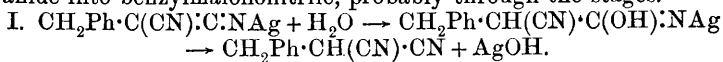
**Alkylmalononitriles and their Derivatives.** By JOHN C. HESSLER (*Amer. Chem. J.*, 1899, 22, 169—198).—The product obtained

by the interaction of ethylic cyanacetate, sodium ethoxide, and ethylic iodide in alcoholic solution (Henry, *Jahresber.*, 1889, 637) contains 70 per cent. of ethylic ethylcyanacetate and 30 per cent. of ethylic diethylcyanacetate; the amount of the latter is diminished by carrying out the action in ethereal solution. On leaving the crude mixture in contact with aqueous ammonia during 24 hours, ethylcyanacetamide (Henry, *loc. cit.*) is formed, whilst the *ethylic diethylcyanacetate* is not acted on and can be isolated by distilling under diminished pressure; it is a colourless liquid which boils at  $110-112^{\circ}$  under 24 mm., and at  $215-216^{\circ}$  under ordinary pressure, and when heated with concentrated hydrochloric acid at  $100^{\circ}$  yields diethylcyanacetic acid (Hesse, Abstr., 1897, i, 16). *Ethylcyanacetic acid*,  $\text{CN}\cdot\text{CHEt}\cdot\text{COOH}$ , prepared by treating crude ethylic ethylcyanacetate in ethereal solution with aqueous caustic soda, which, under these conditions, does not act on the diethylcyanacetate present, is a hygroscopic liquid; it boils at  $160-161^{\circ}$  under 24 mm., but when distilled under the ordinary pressure is decomposed into carbonic anhydride and butyronitrile; the *silver* salt,  $\text{C}_5\text{H}_9\text{O}_2\text{NAg}$ , is a white, crystalline powder which blackens on keeping. Pure ethylic ethylcyanacetate,  $\text{CN}\cdot\text{CHEt}\cdot\text{COOEt}$ , prepared by warming the silver salt with ethylic iodide, boils at  $207-209^{\circ}$  and has a sp. gr. 0.985 at  $22.3^{\circ}$ .

When ethylic cyanacetate is treated with benzylic chloride (1 mol.) and sodium according to the Conrad-Limpach method, ethylic dibenzylcyanacetate (compare Cassirer, Abstr., 1893, i, 16) is formed together with about 20 per cent. of *ethylic benzylicyanacetate*,  $\text{CN}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{COOEt}$ ; the latter, however, is the principal product of the action of benzylic chloride on dry ethylic sodiocyanacetate at  $80^{\circ}$ . It is a colourless oil which boils at  $176-183^{\circ}$  under 20 mm. pressure, and is not acted on by aqueous sodium carbonate; with cold caustic soda, it yields sodium benzylicyanacetate, but, on warming, sodium benzylmalonate is formed. Ethylic dibenzylcyanacetate is a viscid, yellow syrup which boils at  $237^{\circ}$  under 25 mm. pressure, and solidifies after several weeks to large, colourless crystals melting at  $33^{\circ}$  (compare Cassirer, *loc. cit.*).

*Benzylcyanacetamide*,  $\text{CN}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the action of ammonia on ethylic benzylicyanacetate, crystallises from alcohol in large, colourless prisms and melts at  $130^{\circ}$ ; it is stable in presence of aqueous sodium carbonate, but is rapidly hydrolysed by caustic soda. When distilled with phosphorus pentachloride under 20 mm. pressure, it yields *benzylmalononitrile*,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CN})_2$ , which crystallises from alcohol in large, white rhombohedra, from water or light petroleum in needles, melts at  $91^{\circ}$ , and boils at  $174^{\circ}$  under 23 mm. pressure; when treated with sodium in benzene solution, it yields the *sodium* derivative,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CN})\text{:C:NNa}$ , in the form of a white, amorphous powder, which is decomposed by water, regenerating benzylmalonitrile, and when heated at  $120^{\circ}$  under 20 mm. pressure yields hydrocinnamonitrile together with sodium cyanide and the so-called azulmic acid. *Silver benzylmalononitrile*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CN})\text{:C:NAg}$ , prepared by adding dilute caustic potash drop by drop to a mixture of benzylmalononitrile and silver nitrate dissolved in 66 per cent. alcohol,

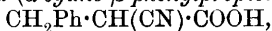
is a white, amorphous powder which is stable in dry, but is rapidly decomposed by moist air; when heated at  $80^{\circ}$ , it yields silver cyanide and a resinous substance, and is converted by aqueous potassium cyanide into benzylmalononitrile, probably through the stages.



Ethylmalononitrile (compare Henry, *loc. cit.*),  $\text{CHEt}(\text{CN})_2$ , prepared from ethylcyanacetamide and phosphorus pentachloride, is a colourless oil which boils at  $90\text{--}91^{\circ}$  under 20 mm. and at  $200^{\circ}$  under ordinary pressure, and darkens on keeping; it dissolves in cold caustic soda, yielding sodium ethylcyanacetate, which, on heating, is converted into sodium ethylmalonate. It is only slowly acted on by sodium in ethereal or benzene solution; neither the sodium nor the silver derivative could be isolated.

Dibenzylmalononitrile,\*  $\text{C}(\text{CH}_2\text{Ph})_2(\text{CN})_2$ , prepared by the action of alcoholic sodium ethoxide and benzylic chloride on malononitrile dissolved in absolute alcohol, is a white, crystalline solid which melts at  $131^{\circ}$  and is not acted on by aqueous alkalis. A poor yield of a mixture of mono- and di-benzylmalononitriles is obtained on heating dry sodium malononitrile with benzylic chloride.

*Benzylcyanacetic acid* ( $\alpha$ -cyano- $\beta$ -phenylpropionic acid),



prepared by hydrolysing its ethylic salt, is a white, crystalline solid which melts at  $101\text{--}102^{\circ}$  and, when distilled, decomposes into carbonic anhydride and hydrocinnamonitrile; the *silver* salt is a heavy, white solid which darkens slowly in the light and melts and decomposes at  $140^{\circ}$ .

*Benzoylbenzylmalononitrile*,  $\text{CH}_2\text{Ph}\cdot\text{CBz}(\text{CN})_2$ , separates as a crystalline mass on mixing benzoic chloride with sodium benzylmalononitrile in cold absolute ether; it is sparingly soluble in light petroleum, melts at  $100^{\circ}$ , and is not acted on by water or aqueous sodium carbonate, but is decomposed by alcohol or aqueous sodium hydroxide, the benzoyl group being removed.

*Bromobenzylmalononitrile*,  $\text{CH}_2\text{Ph}\cdot\text{CBr}(\text{CN})_2$ , prepared by adding sodium benzylmalononitrile to bromine dissolved in ether, crystallises from alcohol in thin plates with serrated edges, from light petroleum in needles, and melts at  $119\text{--}120^{\circ}$ ; it is not acted on by aqueous caustic soda, but when heated alone decomposes, the distillate apparently consisting of benzylidenemalononitrile.

*Ethylic benzyldicyanacetate*,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CN})_2\cdot\text{COOEt}$ , formed by the interaction of sodium benzylmalononitrile and ethylic chloroformate in cold absolute ether, crystallises from a mixture of ether and light petroleum in large, colourless prisms, and melts at  $44\text{--}45^{\circ}$ .

*Methylbenzylmalononitrile*,  $\text{CH}_2\text{Ph}\cdot\text{CMe}(\text{CN})_2$ , obtained by the action of methylic iodide on the silver or sodium derivative of benzylmalononitrile, crystallises from water in needles and from light petroleum in large prisms, and melts at  $94\text{--}95^{\circ}$ . When, however, methylic iodide is added to an alcoholic solution of benzyl-

\* Dibenzylmalononitrile has been prepared by Errera and Berté (*Abstr.*, 1897, i, 18), but no reference is made to this fact in the paper.—W. A. D.

malononitrile and sodium ethoxide, *benzylmethylcyanacetimidoethyl ether*,  $\text{CH}_2\text{Ph}\cdot\text{CMe}(\text{CN})\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , is formed instead of the expected nitrile; it boils at  $170^\circ$  under 22 mm., at  $156^\circ$  under 9 mm. pressure, and can also be obtained by the action of alcoholic sodium ethoxide on benzylmethylmalononitrile. *Benzylethylcyanacetimidoethyl ether*,  $\text{CH}_2\text{Ph}\cdot\text{CEt}(\text{CN})\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , prepared from either ethyl- or benzylmalononitrile, boils at  $170^\circ$  under 22 mm. pressure.

Phenylacetimidoethyl ether,  $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , prepared from the hydrochloride by Bushong's method (Abstr., 1896, i, 546), boils at  $105\text{--}106^\circ$  under 10 mm. pressure (compare Lückenbach, Abstr., 1884, 1134); *ethylic monimidomalonate*,  $\text{COOEt}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}$ , prepared by adding the hydrochloride obtained by Pinner's method (Abstr., 1895, i, 264) to 10 per cent. aqueous caustic potash, distils without change under diminished pressure, but decomposes when heated at  $165^\circ$ .

W. A. D.

**Synthesis of Unsaturated Dicarboxylic Acids from Ketones and Diethylic Succinate.** By HANS STOBBE (*Annalen*, 1899, 308, 67—88. Compare Abstr., 1896, i, 234, and 1897, i, 192).—In a former paper (Abstr., 1895, i, 142), the author has shown that when acetophenone and methyl ethyl ketone undergo condensation with diethylic succinate, two isomeric acids are produced in each case. Those melting at the higher temperature decompose on fusion, and were regarded as substituted itaconic acids, for example,  $\gamma$ -methylphenylitaconic acid,  $\text{CMePh}\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$ , from acetophenone; the isomeric acids, melting without decomposition, were called aticonic acids, and were looked upon as being stereoisomeric. Subsequent investigation, however, has rendered it more probable that they are structurally isomeric, having the unsaturated linking in the  $\gamma\delta$ -position relative to the first carboxylic group; this refers then to pyrotartaric acid, and the substance formerly called phenylmethylitaconic acid becomes  $\gamma$ -phenyl- $\gamma$ -methylenepyrotartaric acid,  $\text{CH}_2\cdot\text{CPh}\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$ . The class name  $\gamma$ -alkylenepyrotartaric acid is chosen to represent those acids which do not decompose on fusion (compare Fittig, this vol., i, 332).

The following abstracts contain descriptions of the acids obtained by condensing other ketones with diethylic succinate. According to the constitution of the ketone, condensation gives rise either to a single itaconic acid, a single alkylenepyrotartaric acid, or a mixture of both acids. Thus, benzophenone yields  $\gamma$ -diphenylitaconic acid as sole product, whilst acetophenone gives rise to  $\gamma$ -phenyl- $\gamma$ -methylitaconic,  $\gamma$ -phenyl- $\gamma$ -methylisotaconic, and  $\gamma$ -phenyl- $\gamma$ -methylenepyrotartaric acids; deoxybenzoin and dibenzyl ketone yield  $\gamma$ -phenyl- $\gamma$ -benzylidenepyrotartaric acid and  $\gamma$ -benzyl- $\gamma$ -benzylidenepyrotartaric acid respectively.

Theoretical considerations occupy the remaining portion of the paper.

M. O. F.

**Condensation of Benzophenone with Diethylic Succinate.** By HANS STOBBE (*Annalen*, 1899, 308, 89—114. Compare Abstr., 1896, i, 234).—Ethylic hydrogen diphenylitaconate, obtained by condensing benzophenone with diethylic succinate under the influence of

sodium ethoxide, has been already described (*loc. cit.*); the *sodium* and *calcium* salts are anhydrous. *Ethylic β-bromo-γ-diphenylparaconate*, formed when the foregoing ethereal salt is treated with bromine water, crystallises from light petroleum in lustrous prisms, and melts at 95·5—96·5°. *Diphenylitaconic acid* crystallises from benzene in needles containing  $\frac{1}{2}$  mol. of the solvent, whilst ether deposits it in lustrous, monoclinic crystals, containing 1 mol. of the solvent; the *sodium* salt contains  $2\text{H}_2\text{O}$ , and the *calcium*, *barium*, and *silver* salts are anhydrous.

[With PAUL KOHLMANN.]—The *anhydride* of  $\gamma$ -diphenylitaconic acid crystallises from petroleum in large, colourless prisms, and melts at 151—152°.

$\gamma$ -*Diphenylpyrotartaric acid*,  $\text{CHPh}_2 \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared by reducing diphenylitaconic acid with sodium amalgam, separates from water in fibrous crystals containing  $1\text{H}_2\text{O}$ ; in this condition, it melts indefinitely between 145° and 180°, but the anhydrous acid melts at 180—184°. The *calcium* salt contains  $2\text{H}_2\text{O}$ , and the *barium* salt  $1\text{H}_2\text{O}$ , whilst the *silver* salt is anhydrous.

When diphenylitaconic acid is oxidised in alkaline solution with potassium permanganate, benzophenone is regenerated; the other products are oxalic and benzoic acids.

[With MAX NOETZEL.]— $\gamma$ -*Diphenylaconic* ( $\gamma$ -*diphenylcrotonolactone-carboxylic*) acid,  $\text{O} < \begin{array}{c} \text{CPh}_2 \cdot \text{C} \cdot \text{COOH} \\ \text{CO} - \text{CH} \end{array}$ , prepared by the action of hot water on  $\beta$ -bromo- $\gamma$ -diphenylparaconic acid (*loc. cit.*), separates from water in crystals containing  $1\text{H}_2\text{O}$ , and melting at 100—101°; the anhydrous acid, obtained by recrystallisation from benzene or carbon bisulphide, melts at 138—139°. The *calcium* and *silver* salts are anhydrous, but the *barium* salt contains  $\frac{3}{2}\text{H}_2\text{O}$ .

$\gamma$ -*Diphenylcrotonolactone*,  $\begin{array}{c} \text{CH} \cdot \text{CPh}_2 \\ \text{CH} - \text{CO} \end{array} > \text{O}$ , formed on elimination of carbonic anhydride from the foregoing acid consequent on protracted treatment with boiling water, crystallises from light petroleum in large prisms and melts at 130—131°; it dissolves in hot sodium carbonate, and the solution reduces potassium permanganate. M. O. F.

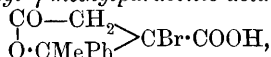
**Condensation of Acetophenone with Diethylic Succinate.** By HANS STOBBE (*Annalen*, 1899, 308, 114—155. Compare *Abstr.*, 1895, i, 142).— $\gamma$ -Phenyl- $\gamma$ -methylitaconic acid crystallises from chloroform in a network of plates belonging to the monoclinic system; it melts and decomposes at 171° (compare *loc. cit.*). The acid is sparingly soluble in cold water and requires 580 parts of benzene at 17° to dissolve it. The *anhydride* crystallises from carbon bisulphide in needles or plates, and melts at 114°. Oxidation with potassium permanganate in alkaline solution resolves  $\gamma$ -phenyl- $\gamma$ -methylitaconic acid into acetophenone and formic, acetic, pyruvic, oxalic, and malonic acids.

$\gamma$ -*Phenyl- $\gamma$ -methylpyrotartaric acid*,  $\text{CHMePh} \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$ , prepared by reducing  $\gamma$ -phenyl- $\gamma$ -methylitaconic acid with sodium amalgam, crystallises from benzene and melts at 144—146·5°; the *calcium* salt forms a gelatinous precipitate, and the *silver* salt resists the action of light.

*cis*- $\beta$ -Bromo- $\gamma$ -phenyl- $\gamma$ -methylparaconic acid melts and decomposes at  $161^\circ$  (compare *loc. cit.*); boiling water converts it into  $\gamma$ -phenyl- $\gamma$ -methylaconic acid, of which the *barium* salt is anhydrous.

$\gamma$ -Phenyl- $\gamma$ -methylisoitaconic acid,  $\text{CMePh}\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$ , produced along with the isomeride on condensing acetophenone with diethylic succinate, crystallises from ether in long needles, and melts at  $183$ — $185^\circ$ , when it decomposes; it dissolves in 475 parts of water at  $17^\circ$ , and in 2000 parts of cold chloroform, but is virtually insoluble in benzene. The *calcium* salt contains  $2\text{H}_2\text{O}$ , and the *barium* salt is anhydrous; the *diethylic* salt boils at  $305$ — $307^\circ$ . The *anhydride* melts at  $138^\circ$ , and then becomes greenish-yellow; it separates from acetic chloride in monoclinic, hemimorphic crystals, and from chloroform and carbon bisulphide in rhombic plates. Phenylmethylisoitaconic acid gives rise to the same products of oxidation as the isomeride.

*trans*- $\beta$ -Bromo- $\gamma$ -phenyl- $\gamma$ -methylparaconic acid,



prepared by the action of bromine on phenylmethylisoitaconic acid, crystallises from benzene in aggregates of transparent prisms and melts at  $129^\circ$ , decomposing slowly at  $147^\circ$ .

[With GEORG HEUN.]—*Ethylic hydrogen- $\gamma$ -phenyl- $\gamma$ -methylisoitaconic acid*,  $\text{CMePh}\cdot\text{C}(\text{COOEt})\cdot\text{CH}_2\cdot\text{COOH}$ , dissolves in 200 parts of boiling water and crystallises in thin leaflets melting at  $110$ — $112^\circ$ ; on adding petroleum to the solution in benzene, it separates in long needles belonging to the rhombic system. The *calcium* and *barium* salts dissolve readily in water, the former containing  $1\text{H}_2\text{O}$ ; the *silver* salt crystallises from water in small prisms and becomes violet when exposed to light. Bromine converts the acid into the *ethylic* salt of *trans*- $\beta$ -bromo- $\gamma$ -phenyl- $\gamma$ -methylparaconic acid, which separates from petroleum in rhombohedral crystals and melts at  $103$ — $104^\circ$ .

$\gamma$ -Phenyl- $\gamma$ -methylenepyrotartaric acid,



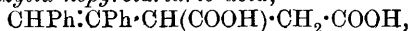
formerly described as phenylmethylaconic acid (*loc. cit.*), melts at  $152$ — $154^\circ$  without decomposing; it is more sparingly soluble in water than the isomeric itaconic acids, but in its solubility in ether it lies between phenylmethylitaconic acid and the isomeride, being six times more soluble than the latter. The *calcium* and *barium* salts are anhydrous. Oxidation converts a portion of the acid into  $\beta$ -benzoylpropionic and oxalic acids, and bromine gives rise to  $\beta$ -bromo- $\beta$ -phenylbutyrolactoneacetic acid,  $\text{CH}_2\cdot\text{C} \begin{array}{c} \text{CBrPh} \\ \text{O}-\text{CO} \end{array} \text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ , which melts

and decomposes at  $177^\circ$ ; when the last-named substance is treated with boiling water, the *lactone* of  $\beta$ -hydroxy- $\beta$ -phenylbutyrolactoneacetic acid,  $\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CPh}-\text{O} \\ \text{CO}-\text{CH}\cdot\text{CH}_2 \end{array} \text{CO}$ , is produced, crystallising in long needles melting at  $144^\circ$ .

M. O. F.

Condensation of Deoxybenzoin with Diethylic Succinate. By HANS STOBBE and KARL RUSSWURM (*Annalen*, 1899, 308, 156—174).

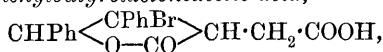
— $\gamma$ -Phenyl- $\gamma$ -benzylidenepyrotartaric acid,





prepared from deoxybenzoin and diethylic succinate, crystallises from dilute aqueous solution in leaflets and melts at 151—152° without decomposing; it separates from benzene in flat needles containing 1 mol. of the solvent. The *barium* salt contains 3H<sub>2</sub>O, the *calcium* and *silver* salts being anhydrous; the *diethylic* salt melts at 39—41° and boils at 230—240°. Oxidation with alkaline potassium permanganate resolves the acid into benzaldehyde and benzoylpropionic acid, along with an acid, C<sub>18</sub>H<sub>14</sub>O<sub>5</sub>, which melts at 203—204°.

*β-Bromo-β-γ-diphenylbutyrolactoneacetic acid*,



obtained by the action of bromine on *γ* phenyl-*γ*-benzylidenepyrotar taric acid, crystallises from chloroform in white, lustrous leaflets, and melts at 144—145°, evolving hydrogen bromide. Hot water converts

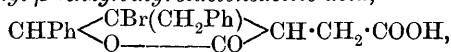
the lactonic acid into the dilactone,  $\begin{array}{c} \text{CHPh} \cdot \text{CPh} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \cdot \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \end{array} \text{CO}$ , the *lactone* of *β*-hydroxy-*βγ*-diphenylbutyrolactoneacetic acid, which crystallises in long, slender needles and melts at 189—191° without decomposing.

Stable *βγ*-diphenylcrotonolactoneacetic acid,  $\begin{array}{c} \text{CHPh} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{O} \text{---} \text{CO} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{COOH}$ ,

is also produced by the action of hot water and alkalis on diphenyl-bromobutyrolactoneacetic acid, and melts at 212—214°, when it becomes red and evolves gas; the *calcium*, *barium*, and *silver* salts are anhydrous.

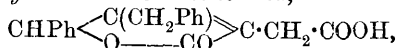
When crude *β*-bromo-*βγ*-diphenylbutyrolactoneacetic acid is re-crystallised from chloroform, the mother liquor contains the lactonic acid, C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>, which melts at 95°, and separates from benzene in crystals containing 1 mol. or 1½ mols. of the solvent; the acid C<sub>18</sub>H<sub>16</sub>O<sub>5</sub> is also present, melting at 169—171·5° and containing ½ mol. of benzene when crystallised from that medium. M. O. F.

**Condensation of Dibenzyl Ketone with Diethylic Succinate.** By HANS STOBBE, KARL RUSSWURM, and JULIUS SCHULZ (*Annalen*, 1899, 308, 175—183. Compare Abstr., 1896, i, 235).—*γ*-Benzyl-*γ*-benzylidenepyrotartaric acid, CHPh·C(CH<sub>2</sub>Ph)·CH(COOH)·CH<sub>2</sub>·COOH, melts at 146—147°; the ethylic *barium* salt crystallises from water in aggregates of small needles, and the ethylic hydrogen salt (*loc. cit.*) obtained by condensing dibenzyl ketone with diethylic succinate, melts at 127·5—129°. The *sodium*, *calcium*, *barium*, and *silver* salts are anhydrous. Oxidation with alkaline potassium permanganate converts the acid into *δ*-phenyl-lævulic acid, and bromine gives rise to *β*-Bromo-*γ*-phenyl-*β*-benzylbutyrolactoneacetic acid,



which melts at 157—159°, evolving gas.

*γ*-Phenyl-*β*-benzylcrotonolactoneacetic acid,



prepared by the action of a small quantity of hot water on the foregoing bromo-derivative, crystallises from a mixture of benzene and petroleum in needles, and melts at 115—117°; the *calcium* and *silver*

salts are anhydrous. The lactone of  $\beta$ -hydroxy- $\gamma$ -phenyl- $\beta$ -benzyl-butyrolactoneacetic acid,  $\text{CHPh}\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{O}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}$ , crystallises from ether in slender needles, and melts at  $202\text{--}203^\circ$  without decomposing.  
M. O. F.

**Benzylidene Compounds of Hydroxy-Acids.** By W. ALBERDA VAN EKENSTEIN and CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1899, 18, 305—308).—Idonic acid is readily separated from its stereoisomeride, gulonic acid, by treating a solution of their sodium salts with concentrated hydrochloric acid and benzaldehyde; the former acid alone combines with the aldehyde, yielding a dibenzylidene derivative insoluble in aqueous solutions. It was found that very few of the hydroxy-acids combine with benzaldehyde under these conditions; out of a total of 39, only three, namely, *l*-xylonic, *d*-saccharic, and  $\alpha$ -glucoheptonic acids, yielded benzylidene derivatives; Some of the properties of these compounds are tabulated as follows:

Acids.	M. p.	[ $\alpha$ ] <sub>D</sub> , 0.4 per cent. in methyl alcohol.	Solubility mgrm. per 10 c.c. at $17^\circ$ .		
			Water.	Ethyl alcohol.	Methyl alcohol.
Dibenzylidene- <i>l</i> -idonic ...	215°	- 5°	25	30	35
Dibenzylidene- <i>l</i> -xylonic ...	199	- 22	12	54	48
Benzylidene- <i>d</i> -saccharic...	215	+ 84	50	45	70
Benzylidene- $\alpha$ -gluco- heptonic.....	210	- 59	65	60	175

The number of benzylidene residues present in the condensation product is determined by heating the substance with dilute sulphuric acid and phenylhydrazine, and weighing the benzylidenephylhydrazone produced; this process may also be applied to the proximate analysis of the benzylidene derivatives of hexahydric alcohols.

G. T. M.

**Disulphones and Ketosulphones.** By ELMER P. KOHLER and MARGARET B. MACDONALD (*Amer. Chem. J.*, 1899, 22, 219—226).—Aromatic disulphones of the type  $\text{R}\cdot\text{SO}_2\cdot\text{SO}_2\text{R}$  can be prepared by warming sulphonic chlorides with the sodium salt of a sulphinic acid, and sufficient water to form a paste. Ketosulphones are formed when an acidyl chloride is substituted in this reaction for the sulphonic chloride.

*Diparatolylidisulphone*,  $\text{S}_2\text{O}_4(\text{C}_6\text{H}_4\text{Me})_2$ , prepared from paratoluene-sulphonic chloride and sodium paratoluenesulphinate, is insoluble in water or alcohol, sparingly soluble in ether, and moderately soluble in chloroform or boiling benzene; it forms large, monoclinic tables, melts and decomposes at about  $212^\circ$ , and is not acted on by dilute acids and alkalis, although when heated with concentrated caustic potash it yields a mixture of potassium sulphonate and sulphinate.

*Phenylparatolyldisulphone*,  $\text{SO}_2\text{Ph}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared from benzenesulphonic chloride and sodium paratoluenesulphinate, and also from paratoluenesulphonic chloride and sodium benzenesulphinate, crystallises in plates, melts at  $166^\circ$ , and, when heated with aqueous caustic potash, yields potassium benzenesulphonate and sulphinat and potassium paratoluenesulphonate and sulphinat.

*Paratolyparanitroorthotolyldisulphone*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$ , prepared from 3-nitrotoluene-6-sulphonic chloride and sodium paratoluenesulphinate, crystallises from chloroform in stout prisms, and melts at  $154^\circ$ ; in its preparation diparatolyldisulphone is also formed, indicating that some of the chloride interacts with the sulphinat thus:  $\text{NO}_2\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2\text{Cl} + \text{C}_7\text{H}_7\cdot\text{SO}_2\text{Na} = \text{NO}_2\cdot\text{C}_7\text{H}_6\cdot\text{SO}_2\text{Na} + \text{C}_7\text{H}_7\cdot\text{SO}_2\text{Cl}$ .

*Phenylparatolyketosulphone*,  $\text{COPh}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$ , prepared by heating sodium paratoluenesulphinate and benzoic chloride dissolved in ether in a sealed tube at  $110^\circ$  for 72 hours, is a colourless oil which decomposes when distilled and solidifies when left in contact with aqueous sodium carbonate, yielding the hydrate  $\text{C}_7\text{H}_7\cdot\text{SO}_2\cdot\text{CPh}(\text{OH})_2$ ; this crystallises from light petroleum in stout needles and melts at  $80^\circ$ . Both the ketosulphone and its hydrate readily combine with hydrogen cyanide, hydroxylamine, phenylhydrazine, primary amines, and phenols, yielding crystalline products. W. A. D.

**Action of Sulphur Monochloride and Dichloride on Sulphinates, Thiosulphonates, and Mercaptans.** By JULIUS TROEGER and VICTOR HORNING (*J. pr. Chem.*, 1899, [ii], 60, 113—140). — *Benzenesulphonic bisulphide*,  $(\text{C}_6\text{H}_5\cdot\text{SO}_2)_2\text{S}_2$ , prepared by the action of sulphur monochloride on sodium benzenesulphinate suspended in carbon tetrachloride, is a white, crystalline powder, and melts at  $76\text{--}77^\circ$ . The trisulphide (m. p.  $103^\circ$ ) is the chief product when the action takes place in presence of water, or when the above mixture is not cooled sufficiently, and is also produced on attempting to recrystallise the bisulphide from hot alcohol. The action of sulphur monochloride on sodium paratoluenesulphinate gives as the chief product *paratoluenesulphonic bisulphide*,  $(\text{C}_7\text{H}_7\cdot\text{SO}_2)_2\text{S}_2$ , a white powder melting at  $98\text{--}100^\circ$ , together with the monosulphide (Otto and Troeger, *Abstr.*, 1891, 924), which crystallises from benzene in white needles and melts at  $136^\circ$ , and the *trisulphide*, which forms minute, white crystals and melts at  $180^\circ$ . The action of sulphur monochloride on sodium orthotoluenesulphinate gives only *orthotoluenesulphonic trisulphide*,  $(\text{C}_7\text{H}_7\cdot\text{SO}_2)_3\text{S}_3$ , which crystallises from acetic acid in white, glistening needles and melts at  $124\text{--}125^\circ$ , and the bisulphide does not appear to be produced. Sodium  $\alpha$ -naphthalenesulphinate similarly gives  $\alpha$ -*naphthalenesulphonic trisulphide*,  $(\text{C}_{10}\text{H}_7\cdot\text{SO}_2)_3\text{S}_3$ , a white, microcrystalline powder, which melts and chars at  $167\text{--}168^\circ$  and dissolves in benzene or ethylic acetate, but not in water or ether;  $\beta$ -*naphthalenesulphonic trisulphide* is a white, crystalline powder which melts and decomposes at  $130\text{--}132^\circ$ , dissolves readily in benzene or ethylic acetate, less readily in alcohol or chloroform, but not in water or light petroleum; the bisulphides could not be prepared.

The action of sulphur dichloride on sodium benzenesulphinate gives the monosulphide,  $(\text{C}_6\text{H}_5\cdot\text{SO}_2)_2\text{S}$ , melting at  $133^\circ$ . *Paratoluenesulphonic sulphide*,  $(\text{C}_7\text{H}_7\cdot\text{SO}_2)_2\text{S}$ , prepared similarly, crystallises from

glacial acetic acid in white needles, melts at  $136^{\circ}$ , dissolves readily in benzene or ethylic acetate, less readily in alcohol, but not in ether or water; it decomposes when kept. *Orthotoluenesulphonic sulphide* crystallises from acetic acid in white, glistening, monoclinic prisms, melts at  $138$ — $139^{\circ}$ , and dissolves in benzene, alcohol, or chloroform, but not in water.  *$\alpha$ -Naphthalenesulphonic sulphide*,  $(C_{10}H_7 \cdot SO_2)_2S$ , crystallises from acetic acid in glistening, pointed or columnar crystals, melts at  $179$ — $180^{\circ}$ , dissolves readily in benzene or ethylic acetate, and slightly in alcohol, but not in water or ether.  *$\beta$ -Naphthalenesulphonic sulphide* crystallises from acetic acid in minute, white crystals, melts at  $153^{\circ}$ , dissolves readily in benzene, ethylic acetate, or chloroform, and slightly in alcohol, but not in water.

*Benzenesulphonic tetrasulphide*,  $(C_6H_5 \cdot SO_2)_2S_4$ , prepared by the action of sulphur monochloride on potassium benzenethiosulphonate, crystallises from acetic acid in minute, white crystals, melts at  $84$ — $85^{\circ}$ , dissolves readily in benzene or ethylic acetate, and less readily in alcohol, but not in water. *Paratoluenesulphonic tetrasulphide*,  $(C_7H_7 \cdot SO_2)_2S_4$ , crystallises from acetic acid in white needles, melts at  $108^{\circ}$ , dissolves readily in benzene or ethylic acetate, and less readily in alcohol, but not in water. *Orthotoluenesulphonic tetrasulphide* was obtained as a pale yellow oil which did not crystallise.  *$\alpha$ -Naphthalenesulphonic tetrasulphide*,  $(C_{10}H_7 \cdot SO_2)_2S_4$ , crystallises from acetic acid in white, microscopic crystals, melts at  $148^{\circ}$ , and dissolves in the ordinary solvents.  *$\beta$ -Naphthalenesulphonic tetrasulphide* crystallises from acetic acid as a white powder, melts at  $90$ — $94^{\circ}$ , and dissolves in the ordinary solvents.

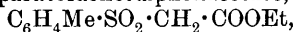
The action of sulphur dichloride on potassium benzenethiosulphonate, potassium para- and ortho-toluenethiosulphonate, and potassium  $\alpha$ - and  $\beta$ -naphthalenethiosulphonate, gave in each case the trisulphide already described.

*Phenyl trisulphide*,  $Ph_2S_3$ , prepared by the action of sulphur dichloride on phenylic mercaptan, is a golden-yellow, mobile oil, with a faint odour; it dissolves readily in benzene or ether, and less readily in alcohol, but not in water. *Paratolylic trisulphide* separates from alcohol as a white, crystalline powder, melts at  $76$ — $77^{\circ}$ , and dissolves in benzene but not in water. *Orthotolylic trisulphide* was obtained as a yellow oil, heavier than water.  *$\alpha$ -Naphthyl trisulphide*,  $(C_{10}H_7)_2S_3$ , prepared by the action of sulphur monochloride on  $\alpha$ -naphthyl mercaptan, crystallises from acetic acid in fine-grained, yellow rhombohedra, melts at  $102^{\circ}$ , dissolves readily in benzene or ethylic acetate, and less readily in chloroform or light petroleum, but not in water.  *$\alpha$ -Naphthyl trisulphide*,  $(C_{10}H_7)_2S_3$ , separates from acetic acid in pale yellow, microscopic crystals, and melts at  $74$ — $75^{\circ}$ .  *$\beta$ -Naphthyl trisulphide* crystallises from acetic acid as a pale yellow powder, melts at  $100$ — $101^{\circ}$ , and dissolves in the ordinary solvents.  *$\beta$ -Naphthyl trisulphide* separates from acetic acid as a fine, white, amorphous powder, melts at  $108$ — $109^{\circ}$ , and dissolves in benzene or ethylic acetate, but not in water.

*Amylic tetrasulphide*,  $(C_5H_{11})_2S_4$ , prepared by the action of sulphur monochloride on amylic mercaptan, is a mobile, light yellow oil, soluble in benzene, ether, or alcohol, but insoluble in water. *Amylic*

*trisulphide*,  $(C_5H_{11})_2S_3$ , prepared by the action of sulphur dichloride on the mercaptan, is a golden-yellow, mobile oil of disagreeable odour, which dissolves in the ordinary solvents. T. M. L.

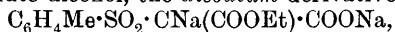
**Action of Sulphonic Chlorides on the Metallic Derivatives of Etheral Salts of Ketonic Acids.** By ELMER P. KOHLER and MARGARET B. MACDONALD (*Amer. Chem. J.*, 1899, **22**, 227—239).—When paratoluenesulphonic chloride (1 mol.) is digested with ethylic sodacetoacetate ( $1\frac{1}{2}$  mols.) in ethereal solution for 1 hour on the water-bath, the principal products are sodium paratoluenesulphinate and symmetrical diethylic diacetylsuccinate, but ethylic acetoacetate, chloracetoacetate, and paratoluenesulphonacetate,



are also formed; it is probable that the first action is the formation of sodium paratoluenesulphinate and ethylic chloracetoacetate, a portion of the latter then interacting with unchanged ethylic sodacetoacetate to form diethylic diacetylsuccinate, whilst the remainder unites with the sodium paratoluenesulphinate, yielding ethylic acetate and paratoluenesulphonacetate. Ethylic chloracetoacetate, however, does not act on sodium paratoluenesulphinate dissolved in benzene or ether, but in presence of alcohol, ethylic acetate and paratoluenesulphonacetate are rapidly formed at the ordinary temperature; the action probably takes place in two stages: I.  $CHClAc \cdot COOEt + C_6H_4Me \cdot SO_2Na = NaCl + C_6H_4Me \cdot SO_2 \cdot CHAc \cdot COOEt$ . II.  $C_6H_4Me \cdot SO_2 \cdot CHAc \cdot COOEt + EtOH = C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot COOEt + CH_3 \cdot COOEt$ . When the mixture is warmed, the action takes place differently, the sulphinate being oxidised to sulphonate, whilst ethylic acetoacetate is formed.

The *ethylic paratoluenesulphonacetoacetate*, formed according to equation I, could not be isolated; the sodium derivative was obtained, however, in small amount, together with sodium paratoluenesulphinate, diethylic diacetylsuccinate, sodium mercaptide, and ethylic acetoacetate, on boiling an ethereal solution of equivalent quantities of ethylic sodacetoacetate and ethylic paratoluenethiosulphonate,  $C_6H_4Me \cdot SO_2 \cdot SEt$ , for 30—40 hours, when it separated as a hard, granular deposit. It is rapidly decomposed by water into sodium acetate and ethylic paratoluenesulphonacetate, whilst the sodium derivative,  $C_6H_4Me \cdot SO_2 \cdot CHNa \cdot COOEt$ , of the latter, together with ethylic acetate, are formed when it is treated with cold absolute alcohol; aqueous and alcoholic potash convert it into tolylmethylsulphone.

When a mixture of ethylic malonate, paratoluenesulphonic chloride, and sodium ethoxide in ethereal solution is heated on the water-bath for several hours, the principal products are ethylic ethylenetetracarboxylate and sodium paratoluenesulphinate; ethylic paratoluenesulphonosodacetate is also obtained, probably owing to the interaction of the paratoluenesulphinate with ethylic chloromalonate and subsequent hydrolysis of the *ethylic paratoluenesulphonomalonnate*,  $C_6H_4Me \cdot SO_2 \cdot CH(COOEt)_2$ , formed. This agrees with the fact that, when paratoluenesulphonic chloride is shaken with ethylic disodiummalonnate in absolute alcohol, the *disodium* derivative,



of monethylic paratoluenesulphonomalonnate is obtained ; on acidifying an aqueous solution of the latter with hydrochloric acid, carbonic anhydride and ethylic paratoluenesulphonacetate are formed.

W. A. D.

**Replacement of several Hydrogen Atoms in Benzene by means of Mercury.** By LEONE PESCI (*Real. Accad. dei Lincei*, 1899, 8, 130—133).—*Dimercuriobenzene acetate*,  $C_6H_4Hg_2(OAc)_2$ , obtained by the action of mercury diphenyl on mercuric acetate, separates from dilute acetic acid in the form of mammillary aggregates of microscopic crystals which are insoluble in water, but dissolve in boiling alcohol or benzene ; it decomposes without melting at about  $230^\circ$ . It is readily soluble in ammoniacal ammonium acetate solution, giving a liquid from which it is precipitated unchanged by the addition of acetic acid. Its solution yields, not mercury sulphide, but a white precipitate when treated with hydrogen sulphide or alkali sulphides, and it is completely soluble in sodium thiosulphate solution.

*Dimercuriobenzene hydroxide*,  $C_6H_4Hg_2(OH)_2$ , prepared by the action of potassium hydroxide on the acetate, is a white powder composed of mammiform, microscopic crystals which have an alkaline reaction and are insoluble in the ordinary solvents. It deflagrates energetically at a high temperature.

*Trimercuriobenzene acetate*,  $C_6H_3Hg_3(OAc)_3$ , obtained from mercury diphenyl and mercuric acetate, forms a white precipitate composed of very small mammillary crystals, and is insoluble in the ordinary solvents, but dissolves slightly in boiling dilute acetic acid. It decomposes without melting at a high temperature, and with sodium thiosulphate behaves like dimercuriobenzene acetate.

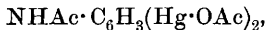
*Trimercuriobenzene hydroxide*,  $C_6H_3Hg_3(OH)_3$ , is a pulverulent substance consisting of very small crystals insoluble in the ordinary solvents ; it does not melt, but at a high temperature decomposes with intense deflagration.

*Tetramercuriobenzene acetate*,  $C_6H_2Hg_4(OAc)_4$ , is a white, powdery product insoluble in the ordinary solvents ; on heating, it decomposes without melting, and behaves like the preceding acetates with respect to sodium thiosulphate.

*Tetramercuriobenzene hydroxide*,  $C_6H_2Hg_4(OH)_4$ , is a pale yellow, amorphous powder which has an alkaline reaction, is insoluble in the ordinary solvents, and deflagrates strongly at a high temperature.

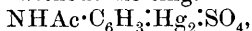
T. H. P.

**Action of Acetanilide on Mercuric Acetate.** By LEONE PESCI (*Chem. Zeit.*, 1899, 23, 58—59. Compare Abstr., 1895, i, 357, 358 ; 1898, i, 648).—2 : 4-*Dimercurioacetanilide acetate*,



is formed when an intimate mixture of mercuric acetate (2 mols.) and acetanilide (1 mol.) is heated at  $114$ — $115^\circ$  until the mixture is completely fused, then kept at this temperature for 1 hour, and finally at  $100^\circ$  for 2 hours. If mixed while still hot with twice its volume of hot water and then allowed to cool slowly, the acetate is obtained in colourless tetrahedra melting at  $220^\circ$ . It usually separates from its

aqueous solutions as a gelatinous mass which slowly crystallises. The *hydroxide*,  $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{Hg} \cdot \text{OH})_2$ , forms a white, insoluble powder decomposing above  $280^\circ$  without melting. The *sulphate*,



crystallises in colourless needles, is insoluble in water or alcohol, but dissolves in warm, dilute acetic acid. J. J. S.

**Electrolysis of Benzoin and of Benzil.** By JOSEPH H. JAMES (*J. Amer. Chem. Soc.*, 1899, 21, 889—910).—The electrolytic oxidation of benzoin in alcoholic sodium hydroxide gives the maximum yield of benzoic acid when a normal current density of 0.25 ampère is employed; with higher densities, less acid and more tarry matter are formed. In alcoholic sulphuric acid solution, a density of 0.5 ampère is required in order to bring about oxidation, the products being the same as in the alkaline solution. In alcoholic hydrogen chloride solution with a density of 1 ampère, the products are benzoic acid and benzil, but when currents of higher density are employed, benzil alone is formed.

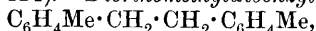
The electrolytic reduction of benzoin in both alcoholic sulphuric acid and alcoholic hydrogen chloride solution gives rise to small quantities of a crystalline compound melting at  $205\text{--}206^\circ$ , the composition of which could not be determined. The oxidation of benzil in alcoholic sodium hydroxide solution yields no definite products, but in alcoholic sulphuric acid solution benzoic acid (14.5 per cent.) may be obtained; in hydrogen chloride solution no change takes place when a current of 1 ampère is employed, and on increasing the density to 7 ampères only tarry products are formed.

By the electrolytic reduction of benzil in alcoholic sulphuric acid, benzoin and a small amount of the substance melting at  $205\text{--}206^\circ$  are produced; benzoin is also formed when an alcoholic hydrogen chloride solution is employed, but no definite products can be isolated when the reduction takes place in alcoholic sodium hydroxide solution. J. J. S.

**Phenylhydrazones of Benzoin.** By ALEXANDER SMITH (*Amer. Chem. J.*, 1899, 22, 198—207).—The author confirms Smith and Ransome's statement (*Abstr.*, 1894, i, 293), which Freer (*Amer. Chem. J.*, 1899, 21, 14) has recently called in question, that benzoin- $\beta$ -phenylhydrazone is converted into the  $\alpha$ -compound when boiled with alcoholic phenylhydrazine. The " $\gamma$ -phenylhydrazone," obtained by Freer (this vol., i, 357) by the action of benzoic chloride on an ethereal solution of the  $\beta$ -isomeride, is in reality benzanilide, ammonium chloride and benzil being also formed. Contrary to Freer's statement, the  $\alpha$ -phenylhydrazone, when treated with benzoic chloride at the ordinary temperature, yields the same products as the  $\beta$ -compound, and when oxidised with nitrous anhydride gives rise to a considerable quantity of the red substance, melting at  $137^\circ$ , described by Freer as being formed only from the  $\beta$ -hydrazone. It thus appears either that both the phenylhydrazones of benzoin have the hydrazo-structure, or that, contrary to Freer's assumption, the formation of red compounds by the action of nitrous anhydride may occur in the case of true hydrazones. W. A. D.

**Preparation of Diphenylmethylenedianiline.** By ERNEST NÄGELI (*Bull. Soc. Chim.*, 1899, [iii], 21, 785—786).—Diphenylmethylenedianiline,  $\text{NPh}\cdot\text{CPh}_2$ , is readily prepared by heating together benzophenone, aniline, and finely-powdered fused sodium sulphate for 18—20 hours at the boiling point of the mixture, and fractionally distilling the product. The yield is about 70 per cent. of the theoretical. N. L.

**Action of Potassium Persulphate on Alkyl Groups.** By C. MORITZ and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 2531—2532. Compare this vol., i, 424).—*Diorthomethyldibenzyl*,

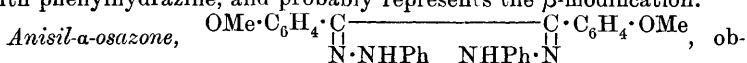


obtained by heating a mixture of orthoxylene and potassium persulphate at  $100^\circ$ , crystallises from alcohol in white, glistening needles and melts at  $66.5^\circ$ . *Diparamethyldibenzyl* forms white, glistening leaflets melting at  $82^\circ$ . *Symmetrical tetramethyldibenzyl*,  $\text{C}_2\text{H}_4(\text{C}_6\text{H}_3\text{Me}_2)_2$ , from mesitylene, melts at  $77$ — $78^\circ$ . *Diethyldibenzyl*,  $\text{C}_2\text{H}_2\text{Et}_2\text{Ph}_2$ , from propylbenzene, forms white, talc-like leaflets and melts at  $88^\circ$ . *Dimetabutyldibenzyl*,  $\text{C}_2\text{H}_4(\text{C}_6\text{H}_4\cdot\text{CMe}_3)_2$ , from 1:3-tertiarybutyltoluene, crystallises in white leaflets and melts at  $149^\circ$ .

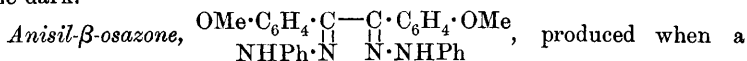
Besides the dibenzyl derivatives, metaxylene and metabutylytoluene yielded the corresponding aldehydes, which were identified by means of their hydrazones; propylbenzene and the para- and meta-xylenes also gave benzoic and terephthalic or isophthalic acids respectively.

When acetic acid (50 grams) was heated on the water-bath for 8 hours with potassium persulphate (120 grams) and water (300 grams), it gave 0.8 gram of succinic acid. G. T. M.

**Oxidation of Aldehydephenylhydrazones to  $\alpha$ -Diketone-osazones.** By HEINRICH BILTZ and ALBERT WIENANDS (*Annalen*, 1899, 308, 1—17. Compare Biltz, this vol., i, 502).—*Cuminilosazone*,  $\text{C}_9(\text{C}_6\text{H}_4\text{Pr}^s)_2(\text{N}_2\text{HPh})_2$ , prepared by passing air through a boiling solution of cumylenephénylhydrazone in alcoholic potash, crystallises from alcohol in aggregates of pale yellow needles and melts at  $253^\circ$ , decomposing slightly; when exposed to direct sunlight, it becomes bright red, regaining its yellow colour in the dark. The substance is identical with the osazone produced by the condensation of cuminal with phenylhydrazine, and probably represents the  $\beta$ -modification.

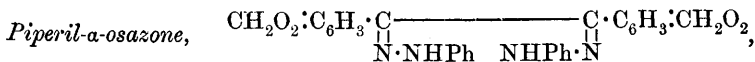


tained on oxidising anisylidenephénylhydrazone in very dilute alcoholic potash by air at  $80^\circ$ , crystallises from chloroform containing alcohol in small, pale yellow needles melting and decomposing at  $171^\circ$ ; it becomes brownish-red when exposed to daylight, but is decolorised in the dark.

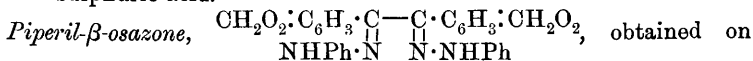


solution of the  $\alpha$ -modification in glacial acetic acid is boiled in a reflux apparatus, separates in small, pale yellow crystals when hot water is added, and melts at  $197^\circ$  without decomposing; it is also formed when anisil is heated with alcoholic phenylhydrazine hydrochloride.





prepared by oxidising a boiling solution of piperonalphenylhydrazone in alcoholic potash, crystallises from a mixture of alcohol and benzene in microscopic needles, and melts at 183—184°, when it decomposes; it is sensitive to light, and forms a yellowish-brown solution in concentrated sulphuric acid.



boiling a solution of the α-osazone in phenylhydrazine, crystallises in small, lemon-yellow needles and melts at 219—220°; it is identical with the osazone prepared from piperil.

*Piperil*,  $\text{C}_2(\text{C}_6\text{H}_3 \cdot \text{CH}_2\text{O}_2)_2\text{O}_2$ , produced when air is passed into a boiling solution of piperoin in aqueous potash during 4 hours, crystallises from a mixture of benzene and alcohol in pale yellow prisms, and melts at 171.5°. The *monoxime* melts at 199°, and yields an *acetate* melting at 124°; the *dioxime* crystallises from alcohol in lustrous prisms and melts at 244°, when it decomposes completely.

*Vanillilosazone*,  $\text{C}_2[\text{C}_6\text{H}_3(\text{OH})(\text{OMe})_2(\text{N}_2\text{HPh})_2]$ , prepared by passing air through a solution of vanillinphenylhydrazone at the ordinary temperature, crystallises from ethylic acetoacetate containing alcohol in microscopic needles, and melts and decomposes at 199—200°; it resists the action of light, and has not been converted into an isomeric modification.

Japp and Klingemann (Trans., 1888, 519) observed the production of diacetylosazone when acetaldehydephenylhydrazone is heated above its melting point for a considerable period; the authors have obtained acetophenone from acetaldehydephenylhydrazone on oxidising the solution in alcoholic potash with air (compare von Pechmann, Abstr., 1898, i, 627).

M. O. F.

**Synthesis of Chrysin.** By T. EMILEWICZ, STANISLAUS VON KOSTANECKI, and JOSEF TAMBOR (*Ber.*, 1899, 32, 2448—2450).—Under the influence of metallic sodium, 2:4:6-trimethoxybenzoylacetophenone is produced from ethylic benzoate and the trimethylic ether of phloracetophenone, alcohol being eliminated; boiling hydriodic acid de-

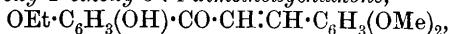
methylates the product, forming chrysin,  $\text{C}_6\text{H}_2(\text{OH})_2 \begin{matrix} \text{O} \cdot \text{CPh} \\ \diagup \quad | \\ \text{CO} \cdot \text{CH} \end{matrix}$ .

2:4:6-Trimethoxybenzoylacetophenone,  $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COPh}$ , crystallises from dilute alcohol in yellowish needles and melts at 100°; ferric chloride develops a red coloration with the alcoholic solution, and bromine in carbon bisulphide gives rise to a *bromo-derivative*,  $\text{C}_{18}\text{H}_{17}\text{O}_5\text{Br}$ , which crystallises in aggregates of needles and melts at 98—99°.

M. O. F.

**Alkyl Ethers of 3:3':4'-Trihydroxybenzylidenecoumaranone.** By STANISLAUS VON KOSTANECKI and A. RÓZYCKI (*Ber.*, 1899, 32, 2257—2260).—Emilewicz and von Kostanecki (this vol., i, 368), by condensing resacetophenone ethylic ether with piperonal, obtained 3-ethoxypiperonalcoumaranone, instead of the isomeric 3-ethoxy-3':4'-methylenedioxyflavone, and it is now found that if methyl- and ethyl-

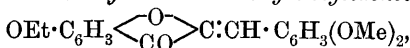
vanillin is substituted for piperonal, the reaction proceeds in a similar way. *2'-Hydroxy-4'-ethoxy-3 : 4-dimethoxychalkone*,



prepared from resacetophenone ethylic ether and methylvanillin in alcoholic sodium hydroxide solution, separates from alcohol or glacial acetic acid in yellow needles melting at 124—125°, which are coloured red by concentrated sulphuric acid, forming a yellow solution. The *acetyl* derivative separates from alcohol in light yellow needles and melts at 106°, and its *dibromide*,

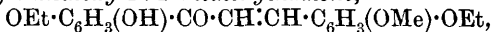


forms a crystalline powder and melts with evolution of gas at 112—114°; when treated with alcoholic potassium hydroxide, this dibromide yields *3'-ethoxy-3 : 4-dimethoxybenzylidenecoumaranone*,



crystallising from alcohol in yellow needles melting at 148—149°, and forming a reddish-yellow solution in concentrated sulphuric acid; when treated with an alcoholic solution of sodium ethoxide, it is transformed into a resin insoluble in alkalis.

*2'-Hydroxy-3-methoxy-4 : 4'-diethoxychalkone*,



prepared from ethylvanillin and resacetophenone ethylic ether, separates from alcohol in small, broad, deep yellow prisms melting at 121—122°, which are coloured dark red by concentrated sulphuric acid and form an orange-coloured solution; the *acetyl* compound separates from alcohol in light yellow needles melting at 103—104°, and its *dibromide* forms white, crystalline crusts melting at 107—108°. *3'-Methoxy-3 : 4'-diethoxybenzylidenecoumaranone*,



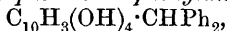
separates from alcohol in intensely yellow needles which melt at 133—135° and are coloured eosin-red by concentrated sulphuric acid.

J. F. T.

**Condensation of Benzhydrols with Paraquinones and with Paraquinonoid Compounds.** By RICHARD MÖHLAU and VOLKMAR KLOPPER (*Ber.*, 1899, **32**, 2146—2159. Compare this vol., i, 62).—The condensation between alcohols and quinones only occurs when the alcohol is a true aromatic secondary alcohol and the quinone a paraquinone or a derivative of the same. The condensation takes place most readily in solution in absolute alcohol, or in a mixture of acetic and sulphuric acids, and, as a rule, an equal number of molecules of the constituents combine together, except in the case of quinone. The condensation products are well-defined, crystalline, coloured compounds; when reduced, they yield quinols, but do not react with phenols, amines, or hydrazines in the same manner as the original quinones.

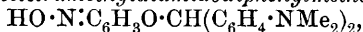
*Quinonebisdiphenylmethane*,  $\text{C}_6\text{H}_2\text{O}_2(\text{CHPh}_2)_2$  [ $\text{O}_2 : (\text{CHPh}_2)_2 = 1 : 4 : 2 : 5$ ], obtained by heating an acetic acid solution of the constituents with 1 c.c. of sulphuric acid (1 : 19) for 12 hours on the water-bath, crystallises from alcohol in long, yellow, glistening prisms,

softening at  $238^{\circ}$  and melting at  $250^{\circ}$ . To obtain a satisfactory yield, it is essential that the materials should be pure. The product is soluble in benzene, sparingly so in alcohol or acetic acid, and insoluble in ether. When reduced, it yields *quinolbisdiphenylmethane*,  $C_6H_2(CHPh_2)_2(OH)_2$ , which crystallises from ether in prisms melting at  $241^{\circ}$  and is only sparingly soluble in alcohol. *Quinonebistetramethyldiamidodiphenylmethane*,  $C_6H_2O_2[CH(C_6H_4 \cdot NMe_2)_2]_2$ , obtained by heating the constituents in absolute alcoholic solution on the water-bath for 6 hours, crystallises from benzene in colourless crystals melting at  $245^{\circ}$ ; on oxidation with potassium permanganate or lead peroxide, it turns bluish-green. The tetramethyldiamidobenzhydrol was obtained by reducing the corresponding ketone with hot amyllic alcohol and sodium.  $\alpha$ -*Naphthaquinonediphenylmethane*,  $C_{10}H_5O_2 \cdot CHPh_2$ , crystallises from alcohol in long, yellow, glistening, acicular prisms melting at  $185^{\circ}$ ; it is sparingly soluble in acetic acid or alcohol, but dissolves more readily in ether, acetone, benzene, light petroleum, or ethylic acetate. When reduced, it yields *diphenyl-1:4-dihydroxy-naphthylmethane*,  $C_{10}H_5(OH)_2 \cdot CHPh_2$ , which, however, could not be obtained in a crystalline form.  $\alpha$ -*Naphthaquinonetetramethyldiamidodiphenylmethane*,  $C_{10}H_5O_2 \cdot CH(C_6H_4 \cdot NMe_2)_2$ , crystallises from ether in violet-red, glistening plates, which soften at  $132^{\circ}$  and melt at  $152^{\circ}$ ; it is only sparingly soluble in alcohol or benzene, but dissolves readily in dilute acids; ammonium sulphide reduces it to the hydro-base, and lead peroxide and hydrochloric acid oxidise it to  $\alpha$ -*naphthaquinone-tetramethyldiamidodiphenylcarbinol*, the chloride of which combines with zinc chloride, yielding a dark blue powder having a constitution,  $3C_{10}H_5O_2 \cdot C(C_6H_4 \cdot NMe_2) : C_6H_4 : NClMe_2 + 2ZnCl_2 + 2H_2O$ , analogous to that of malachite-green. 3':4'-*Dihydroxy- $\alpha$ -naphthaquinonediphenylmethane*,  $C_{10}H_3O_2(OH)_2 \cdot CHPh_2$ , obtained by the condensation of alcoholic solutions of naphthazarin and diphenylcarbinol in the presence of a small quantity of sulphuric acid, crystallises from alcohol in golden-red needles melting at  $196^{\circ}$ , and is only sparingly soluble in alcohol or ether; when reduced with stannous chloride, it yields 1:4:3':4'-*tetrahydroxynaphthalenediphenylmethane*,



which crystallises in pale yellow, prismatic needles melting at  $208^{\circ}$  and only sparingly soluble in most solvents with the exception of benzene. 3':4'-*Dihydroxy- $\alpha$ -naphthaquinonetetramethyldiamidodiphenylmethane*, forms violet crystals melting at  $183^{\circ}$ , is moderately soluble in benzene, ether, or acetic acid, readily soluble in dilute acids, yielding ruby-red solutions, and sparingly in alkalis, giving blue solutions.

*Paranitrosophenoltetramethyldiamidodiphenylmethane*,



obtained by boiling an alcoholic solution of paranitrosophenol and tetramethyldiamidobenzhydrol for 12 hours, crystallises from alcohol in yellow prisms melting at  $217^{\circ}$ ; it is insoluble in alkalis, but dissolves readily in dilute acids.

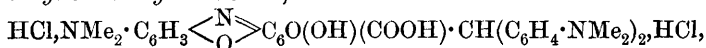
When an alcoholic solution of paranitrosodimethylaniline and diphenylcarbinol is boiled for some hours, the product is Schraube's tetramethyldiamidoazoxybenzene (*Ber.*, 1875, 8, 619; compare Pinnow and Pistor, *Abstr.*, 1893, i, 509), and not, as expected, paranitrosodi-

methylanilidodiphenylmethane. *Paranitrosodimethylanilidotetramethyldiamidodiphenylmethane*,  $O \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NMe}_2 \end{smallmatrix} C_6H_3 \cdot CH(C_6H_4 \cdot NMe_2)_2$ , crystallises from benzene in yellow, acicular prisms melting at  $212^\circ$ , and is readily soluble in alcohol or ether; when reduced, it yields *hexamethyltetramidotriphenylmethane*,  $NH_2 \cdot C_6H_3(NMe_2) \cdot CH(C_6H_4 \cdot NMe_2)_2$ , which crystallises from ether in glistening prisms melting at  $171^\circ$ , and is readily soluble in the ordinary solvents.

Only such quinonimido-dyes condense with benzhydrols as can be regarded as derivatives of paraquinonimide. Indamines and indo-phenols are incapable of condensation. *Tetramethyldiamidodiphenylmethanedimethylnaphthaphenoxazinium chloride hydrochloride*,

$NMe_2Cl \cdot C_6H_3 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_{10}H_5 \cdot CH(C_6H_4 \cdot NMe_2) \cdot C_6H_4 \cdot NMe_2, HCl$ , obtained from alcoholic solutions of the hydrochloride of Meldola's blue and tetramethyldiamidobenzhydrol, forms a bluish-violet powder soluble in alcohol but insoluble in ether. *Tetramethyldiamidodiphenylmethanedimethylhydroxynaphthaphenoxazinium chloride hydrochloride*, obtained from muscarin and tetraphenyldiamidobenzhydrol, forms a dark blue powder with a bronzy lustre, and is soluble in water, yielding a pure blue solution.

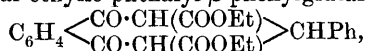
*Tetramethyldiamidodiphenylmethanedimethylamidohydroxyphenoxazone-carboxylic acid hydrochloride*,



obtained from gallocyanin hydrochloride and tetramethyldiamidobenzhydrol, forms a blue powder insoluble in ether but soluble in water, giving a bluish-violet solution, and in dilute acids, yielding a magenta red solution. J. J. S.

**Condensation of Ethylic Phthalate with Ethylic Glutarate.** By W. DIECKMANN (*Ber.*, 1899, 32, 2227—2233).—Ethylic phthalate undergoes condensation with ethylic glutarate in presence of metallic sodium and a few drops of alcohol, yielding *ethylic 1:5-diketophenoheptamethylene-2:4-dicarboxylate* (symmetrical ethylic phthalylglutarate),  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{CH}(\text{COOEt}) \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH}(\text{COOEt}) \end{smallmatrix} CH_2$ , which crystallises in colourless needles melting at  $86-87^\circ$ . It dissolves in dilute aqueous alkalis, but the solution gradually becomes reddish-yellow, and then yields a new acid which has not yet been examined.

When treated with dilute sulphuric acid, ethylic phthalylglutarate yields *1:5-diketophenoheptamethylene*,  $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} CH_2$ , which crystallises in large prisms melting at  $45-46^\circ$ . The *dioxime* melts and decomposes at  $245^\circ$ , whilst the *diphenylhydrazone* melts at  $190^\circ$ . Ethylic  $\beta$ -phenylglutarate reacts with ethylic phthalate in a similar manner, forming *3-phenyl-1:5-diketophenoheptamethylene-2:4-dicarboxylate* (symmetrical ethylic phthalyl- $\beta$ -phenylglutarate),



which crystallises in plates or prisms melting at  $188^\circ$ .

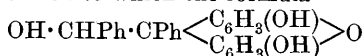
Ethyllic suberate and ethyllic sebacate, unlike the derivatives of glutaric acid, do not react in this manner. A. H.

**Condensation of Benzil and Benzoin with Resorcinol.** By HANS VON LIEBIG (*Ber.*, 1899, **32**, 2332—2335. Compare Japp and Meldrum, *Trans.*, 1899, **75**, 1036).—By heating together benzil and resorcinol for 12 hours at 160°, a substance is produced to which the formula  $C_3Ph_2\left(\begin{smallmatrix} C_6H_3(OH) \\ C_6H_3(OH) \end{smallmatrix} > O\right)_2$  is assigned; it melts at 168°, crystallises from benzene in colourless, narrow, rhombic or needle-shaped plates, and from alcohol in characteristic, regular, four- or six-sided crystals whose corners are joined to the centre by radiating edges, the resulting triangles being striated parallel to the outer edges. Like fluorescein, it readily forms bromo- and nitro-derivatives; it dissolves readily in cold alcohol, ether, or acetone, and in hot benzene or chloroform, very slightly in water or light petroleum, and is soluble in concentrated sulphuric acid with a non-fluorescent, yellow to red colour; alkaline solutions become dark red on exposure to air, but without fluorescence; heating with zinc chloride does not convert the substance into a fluorescent compound. On heating with caustic soda and then acidifying, a crystalline substance,  $C_{38}H_{26}O_6 + 11H_2O$ , is precipitated, which is less soluble in alcohol or ether than the preceding compound and does not dissolve in benzene; it separates from alcohol in well-formed rhombohedra, effloresces in the air, and is converted on drying into the substance melting at 168°, of which it appears to be a hydrate (compare Hantzsch, this vol., i, 400).

The crude condensation product is always coloured red by a dye,  $C_{38}H_{26}O_6 + 1\frac{1}{2}H_2O$ , which forms the chief product if the condensation takes place in presence of zinc chloride; this separates on acidifying an alkaline solution as a dark-red, flocculent precipitate, melts at 114°, dissolves readily in ether, alcohol, or acetone with a green fluorescence, but only slightly in water, benzene, or petroleum, dissolves in caustic soda with a reddish-brown coloration, or in very dilute solution with a rose-red coloration and green fluorescence; it dyes animal fibres red to brown, whilst the nitro-derivative gives yellow to brown, and the bromo-derivative rose-red to red, shades. The acid liquors gradually deposit microscopic needles of a substance,  $C_{38}H_{26}O_6 + 2H_2O$ , which, when dried on the water-bath, gives the substance melting at 168°.

A small quantity of a substance with an intense blue fluorescence was also isolated from the fusion of benzil and resorcinol with zinc chloride; it forms a brown, flocculent precipitate, and dissolves in caustic soda to a dark red solution with a splendid violet-blue fluorescence which gradually disappears, leaving a greenish brown-yellow solution; the solution in ammonia, on the other hand, gradually becomes intensely fluorescent.

By heating together benzoin and resorcinol for 6 hours at 180°, a substance was obtained to which the formula



is assigned; it melts at 134°, crystallises from alcohol in dirty white

needles, dissolves readily in hot ether, benzene, acetone, or chloroform, very slightly in light petroleum or water, and gives a green to brown solution in sulphuric acid; it readily yields nitro- and bromo-derivatives, but does not give a fluorescent substance by fusion with zinc chloride. By the further action of caustic soda on the condensation product, a sodium salt was obtained which crystallised in flakes and showed a beautiful violet-blue shimmer; the corresponding phenol was obtained as a brown resin soluble in alcohol, ether, or benzene with a pale blue fluorescence, and separated from light petroleum in crystalline aggregates. A similar substance was obtained when zinc chloride was added to the mixture before fusion. T. M. L.

**New Method of Preparing Triphenyltrimesic Acid.** By THEODOR LANSER (*Ber.*, 1899, 32, 2478—2481).—An *anhydride*,  $C_{27}H_{16}O_5$ , of triphenyltrimesic acid is prepared by heating phenylpropionic acid with phosphorus oxychloride at  $90^\circ$  until the evolution of hydrogen chloride ceases; when crystallised from a mixture of nitrobenzene and alcohol, it separates in colourless needles and melts at  $256^\circ$ ; it is very insoluble in all organic solvents of low boiling point, but dissolves in cold alcoholic potash to form a potassium salt. 1:3:5-Triphenyltrimesic acid,  $C_6Ph_3(COOH)_3$ , obtained by dissolving the anhydride in hot aqueous potash and then acidifying the solution, crystallises from dilute alcohol and melts at  $257$ — $259^\circ$  (compare Gabriel and Michael, *Abstr.*, 1878, 734, who regarded the compound as phenyltribenzoic acid,  $C_6H_3(C_6H_4 \cdot COOH)_3$ ).

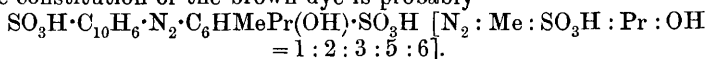
*Trimethylic triphenyltrimesate*,  $C_6Ph_3(COOMe)_3$ , crystallises from dilute alcohol in colourless leaflets and melts at  $121^\circ$ . The *triethylic* salt crystallises in colourless needles and melts at  $129$ — $130^\circ$ .

Another *anhydride* of triphenyltrimesic acid,  $C_6Ph_3:(CO \cdot O \cdot CO)_3:C_6Ph_3$ , obtained by heating the acid to  $200^\circ$  or by treating it with phosphorus oxychloride, crystallises in needles and melts at  $257$ — $259^\circ$ ; it dissolves readily in benzene or in acetic acid and sparingly in alcohol. G. T. M.

**Nitration at Elevated Temperatures.** By ERNEST NÄGELI (*Bull. Soc. Chim.*, 1899, [iii], 21, 786—787).—Attempts to prepare  $\beta$ -nitronaphthalene by heating excess of naphthalene with potassium, or sodium, hydrogen sulphate, and potassium, or sodium, nitrate, at temperatures ranging from  $150^\circ$  to  $360^\circ$  were unsuccessful, the  $\alpha$ -derivative alone being obtained, however the conditions are varied. When aniline is similarly treated, nitration occurs, but a large quantity of a bluish-violet substance is also formed. Benzoic acid and benzaldehyde are readily nitrated by heating with potassium hydrogen sulphate and potassium nitrate, the meta-derivative being in each case the principal product. N. L.

**Action of Diazonium Salts on Thymolsulphonic Acid.** By JAMES H. STEBBINS, jun. (*J. Amer. Chem. Soc.*, 1899, 21, 741—745. Compare *Abstr.*, 1882, 834).—When a solution of diazonaphthionic acid is run into a well cooled alkaline solution of thymolparasulphonic acid, the colour changes to bright red and finally to a reddish-brown;

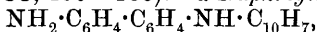
when allowed to remain overnight, then boiled and saturated with sodium chloride, a reddish-brown precipitate is deposited. The solution still contains a crimson-red dye which is extremely readily soluble in water, but is precipitated as its barium salt on the addition of barium chloride; as the amount of the barium salt obtained was small, its constitution has not been determined. The brown precipitate yields a sparingly soluble *barium* salt,  $\text{BaC}_{20}\text{H}_{18}\text{S}_2\text{O}_7\text{N}_2$ , which crystallises from boiling water in orange-coloured, hair-like needles. The constitution of the brown dye is probably



J. J. S.

**Preparation and Properties of Naphthylcarbamides.** By GEORGE YOUNG (*J. pr. Chem.*, 1899, [ii], **60**, 255—256. Compare *Trans.*, 1897, **71**, 1200).—A claim for priority and a criticism of the work of Walther and Wlodkowski (this vol., i, 591). T. M. L.

**Naphthylated Benzidines.** By VICTOR MERZ and H. STRASSER (*J. pr. Chem.*, 1899, [ii], **60**, 159—186).—*α-Naphthylbenzidine*,



is prepared by heating *α*-naphthol with 1·1 to 1·4 mols. benzidine and a little calcium chloride in a stream of carbonic anhydride for 15—18 hours at a temperature rising gradually to 320°. After extracting the unchanged benzidine with much hot water, the *α*-naphthylbenzidine is partially separated from the *α*-dinaphthylbenzidine, which forms 20 per cent. of the crude product, by distilling in a current of superheated steam at 300—330°, or by distilling at 340—380° under 12—14 mm. pressure; the separation is completed by converting the naphthylbenzidine into sulphate and extracting the dinaphthylbenzidine with benzene during 5 or 6 hours in a reflux apparatus; the pure base is finally separated by redistilling, extracting with cold alcohol or ether, and crystallising from benzene. From benzene, it separates in colourless prisms, but from alcohol in glistening plates; it dissolves only slightly in alcohol or ether, but readily in hot aniline, dissolves in 4—4½ parts of hot benzene and in 60 parts at 19°, with a faint bluish fluorescence. It melts at 154·5°, distils at 300—305° under 2—3 mm., at 355—360° under 11—12 mm., at 380—390° under 20—25 mm., and distils with partial decomposition at 500—505° under 755 mm. pressure. The *hydrochloride* and *sulphate* are insoluble and partially decomposed by boiling with water. A solution of the base in concentrated sulphuric acid gives a green coloration with sodium nitrite, whilst potassium nitrate gives an intense characteristic red-brown colour.

When 2 or 4 parts of *α*-naphthol are used for each part of benzidine, the product consisted chiefly of *α*-dinaphthylbenzene, the yields being 67 and 87 per cent. respectively, reckoned on the amount of benzidine used; in the latter case, the excess of naphthol can be recovered by distillation. It crystallises from benzene in colourless, glistening needles, the solubility being 1 in 405 at 24° and 1 in 67·3 at the boiling point; it is only very slightly soluble in alcohol and ether; the solutions show a strong bluish-violet fluorescence, but become reddish to reddish-brown when exposed to air. It melts at 244·5 to 245°, and

boils at 380—390° under 3 mm. pressure, but is partially decomposed when distilled in a current of steam at 400°. A *hydrochloride* was obtained, but the base does not combine with sulphuric acid. A solution of the base in sulphuric acid is coloured dark green by sodium nitrite or potassium nitrate. A certain amount of  $\alpha$ -naphthylene oxide is produced in the preparation of  $\alpha$ -dinaphthylbenzidine.

$\beta$ -Naphthylbenzidine, prepared and purified in a similar manner to the  $\alpha$ -compound, than which it is less soluble, dissolves slightly in ether or in alcohol, and is soluble in 212 parts of benzene at 19°, the solution showing a bluish fluorescence; it crystallises in colourless, rhombic tablets, melts at 150—151°, but when crystallised from benzene becomes vitreous at 144—145°, and crystallises again before melting; it boils at 300—310° under 2—2.5 mm., at 370—373° under 12—13 mm., and distils with partial decomposition at 504—510° under 740 mm. pressure. The salts are sparingly soluble. The colour reactions are similar to those of  $\alpha$ -naphthylbenzidine.

$\beta$ -Dinaphthylbenzidine crystallises from much benzene in flakes, and from aniline in white, pearly, glistening plates; it dissolves in 307—309 parts of benzene at the boiling point, and in 5000—7000 parts at 20°, giving solutions with a bluish-violet fluorescence; it melts at 238.5—239° and boils at 370—380° under 2 to 2.5 mm. pressure; the solution in concentrated sulphuric acid shows a characteristic intense blue coloration with sodium nitrite or potassium nitrate.

$\alpha\beta$ -Dinaphthylbenzidine, prepared by heating  $\alpha$ -naphthylbenzidine with  $\beta$ -naphthol, or  $\beta$ -naphthylbenzidine with  $\alpha$ -naphthol, melts at 200.5—201°, and boils at 365—375° under 2 mm. pressure; it is more soluble than the  $\alpha\alpha$ - and  $\beta\beta$ -isomerides, dissolving in 201 parts of benzene at 24°, and in about 30 parts at the boiling point; it dissolves readily in hot aniline and very slightly in boiling alcohol or ether. The solutions in benzene show a violet fluorescence and become red on exposure to air; the solution in concentrated sulphuric acid is coloured green to bluish-black by nitrous and nitric acids. When heated with hydrochloric acid at 200°, the substance is decomposed into benzidine and  $\alpha$ - and  $\beta$ -naphthol.

T. M. L.

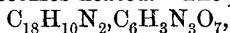
**The Ketones of Anthracene.** By EDUARD LIPPMANN and FRANZ FLEISSNER (*Ber.*, 1899, 32, 2249—2251).—*Benzoylanthracene* or *anthraphenone* is formed in small amount by the action of benzoic chloride on anthracene in presence of aluminium chloride, and crystallises in small needles melting at 138°. *Dibenzoylanthracene* is also formed in the reaction, and crystallises in yellow or brown needles melting above 300°.

A. H.

**Action of Amines and of Amides on Acenaphthenequinone.** By G. AMPOLA and V. RECCHI (*Real Accad. dei Linc.*, 1899, 8, 209—218).—*Acenaphthenephenoparadiazine* ( $\alpha\alpha$ -naphthaquinoxaline),  $C_{12}H_6 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} C_6H_4$ , obtained by the interaction of molecular proportions of orthophenylenediamine hydrochloride and an acetic acid solution of acenaphthenequinone, is a white substance melting at 234° and subliming at a higher temperature in needles. It is soluble in the



ordinary solvents, from which it crystallises in slender needles arranged in glistening leaflets or small spheres. Cold chloroform dissolves it, as also do the concentrated mineral acids; with sulphuric acid, it gives a yellow, and with hydrochloric acid a red, solution and from both of these it is precipitated unchanged by the addition of water. The *hydrochloride*,  $C_{18}H_{10}N_2 \cdot HCl$ , is an intensely yellow substance which is readily decomposed by water and aqueous solvents; in the air, it loses hydrogen chloride and becomes heated. The *picrate*,



crystallises in long, yellow needles melting at  $188^\circ$ ; it is slightly soluble in ether, more so in benzene or glacial acetic acid, but is decomposed by water. The *platinochloride*,  $(C_{18}H_{10}N_2)_2 \cdot H_2PtCl_6$ , separates from alcohol in very small, orange-yellow, glistening crystals which melt and decompose at a very high temperature; it is insoluble in benzene, ether, or acetic acid, and is decomposed by water with liberation of the base. On brominating the base, *dibromo-aa-naphthaquinoxaline*,  $C_{18}H_{10}N_2Br_2$ , is obtained. It separates from glacial acetic acid solution in minute, glistening crystals which dissolve slightly in ether or chloroform; the bromine is removed, leaving the base, on either heating at  $100^\circ$ , or by treating with water, aqueous solvents, alkalis or zinc and acetic acid.

*Dihydroacenaphtheneparadiazine*,  $C_{12}H_6 \begin{smallmatrix} \text{N} \cdot \text{CH}_2 \\ | \\ \text{N} \cdot \text{CH}_2 \end{smallmatrix}$ , prepared from

ethylenediamine and acenaphthenequinone, crystallises from dilute alcohol in long, slender, yellowish needles melting at  $143^\circ$ , and subliming at a higher temperature; it is insoluble in water or alkali solution, fairly soluble in mineral acids, and very soluble in alcohol, ether, or chloroform even in the cold. Its *picrate*,  $C_{14}H_{10}N_2 \cdot C_6H_3N_3O_7$ , crystallises from alcohol in beautiful, orange-yellow plates melting at  $210^\circ$ . The *platinochloride*,  $(C_{14}H_{10}N_2)_2 \cdot H_2PtCl_6$ , separates from acetic acid in small, yellow crystals which char without melting; it is fairly soluble in alcohol and is very readily decomposed by water. *Dibromodihydroacenaphtheneparadiazine*,  $C_{14}H_{10}N_2Br_2$ , separates from chloroform in yellow crystals which are soluble in alcohol or acetic acid and are decomposed by water, aqueous solvents, or alkalis, or by exposure to the air.

By the action of carbamide and fused sodium acetate on acenaph-

thenequinone, a *monourein*,  $\begin{smallmatrix} \text{CO} \\ | \\ C_{10}H_6 \end{smallmatrix} > C \begin{smallmatrix} \text{NH} \\ | \\ \text{NH} \end{smallmatrix} < \text{CO}$ , is obtained which

separates in sparkling white plates melting at  $210^\circ$ . It is insoluble in all the ordinary solvents, and when boiled with water is resolved into carbamide and acenaphthenequinone; it is not attacked by alkalis, but mineral acids and acetic acid decompose it with liberation of quinone. By the action of a large excess of carbamide on acenaph-

thenequinone, a *diurein*,  $C_{12}H_6 \left( \begin{smallmatrix} \text{NH} \\ | \\ \text{NH} \end{smallmatrix} > \text{CO} \right)_2$ , is formed. It is a reddish-brown substance which melts and decomposes at a high temperature and is insoluble in all ordinary solvents except acetic acid, which dissolves it slightly. To concentrated sulphuric acid it gives a red colour and to nitric acid a yellow colour; from both of these

solutions, water precipitates it unchanged. The *dinitrodiurein*,  $C_{14}H_8N_6O_6$ , is a yellow, crystalline powder fairly soluble in acetic acid or alcohol.

T. H. P.

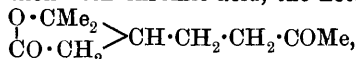
**Structure of Terpenes and Allied Compounds. XXIV. Limonene from Limonene Bromide.** By J. GODLEWSKY and K. ROSHANOWITSCH (*Chem. Centr.*, 1899, i, 1241; from *J. Russ. Chem. Soc.*, 1899, 31, 209—211).—Limonene bromide, melting at  $104^\circ$ , was prepared from carvene and then reduced in alcoholic solution with zinc dust. The limonene so obtained, after distilling in steam, drying over potassium carbonate, and distilling with sodium, boiled at  $177.5^\circ$  under 759 mm. pressure, had a sp. gr. 0.8585 at  $0^\circ/0^\circ$ , 0.8441 at  $20^\circ/20^\circ$ , 0.8584 at  $0^\circ/4^\circ$ , 0.8425 at  $20^\circ/4^\circ$ , and a specific rotatory power  $[\alpha]_D + 125^\circ 36'$  at  $20^\circ$ . By the action of bromine, it forms the original bromide.

E. W. W.

**Structure of Terpenes and Allied Compounds. XXV. Structure of Limonene.** By J. GODLEWSKY (*Chem. Centr.*, 1899, i, 1241; from *J. Russ. Chem. Soc.*, 1899, 31, 211—213).—When limonene free from carvone is oxidised by potassium permanganate, a small quantity of hydroxyterpenylic acid,  $\begin{matrix} \text{COO} \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{OH} \\ | \\ \text{CH}_2 - \text{CH} \cdot \text{CH}_2 \cdot \text{COOH} \end{matrix}$  is formed. This acid is identical with that obtained by oxidising carvone with potassium permanganate (Best, *Abstr.*, 1894, i, 361), and melts at  $174.5^\circ$ . The dilactone of the acid melts at  $129$ — $130^\circ$ , and when treated with potassium hydroxide regenerates hydroxyterpenylic acid.

E. W. W.

**Structure of Terpenes and Allied Compounds. XXII. Lævoterpene Hydrate.** By J. GODLEWSKY (*Chem. Centr.*, 1899, i, 1241; from *J. Russ. Chem. Soc.*, 1899, 31, 203—208).—Lævoterpineol,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH} < \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH} \end{matrix} > \text{CMe}$ , was prepared from turpentine by Flawitzky's method by means of alcoholic sulphuric acid, the mixture being shaken and the product poured into ice. In order to obtain a compound of high rotatory power, the reaction was only allowed to proceed for 10 hours. The terpeneol obtained melts at  $34^\circ$ , and in alcoholic solution has a specific rotatory power  $[\alpha]_D - 95^\circ 28'$  when  $c = 21.4568$ . By oxidising the terpeneol with a 1 per cent. solution of potassium permanganate and then with chromic acid, the ketolactone,



is formed. This compound, which was also prepared by oxidising menthanetriol (Ertshikowsky, *J. Russ. Chem. Soc.*, 28, 132), when dissolved in alcohol, has a specific rotatory power  $[\alpha]_D + 55.3^\circ$  if  $c = 2.6187$ . In the oxidation of lævoterpineol, active terpenylic acid,  $\begin{matrix} \text{O} \cdot \text{CMe}_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{COOH}$ , is also formed.

E. W. W.

**Conversion of Geraniol into Terpeneol (m. p.  $35^\circ$ ).** By KARL STEPHAN (*J. pr. Chem.*, 1899, [ii], 60, 244—254. Compare this vol., i, 68).—When formic acid acts on geraniol at  $0^\circ$  to  $5^\circ$ , the chief product is geranyl formate, whilst on warming terpinene is formed; at a

temperature of  $15^{\circ}$  to  $20^{\circ}$ , however, the product consists largely of terpinyl formate. After the action had proceeded for 12 days, the product is hydrolysed, distilled in a current of steam, and fractionated under 13 mm. pressure; the fraction of lowest boiling point had the characteristic odour of terpinene, but the nitrite could not be prepared; 72 per cent. of the substance, however, distilled between  $102^{\circ}$  and  $104^{\circ}$  and solidified on cooling; the crystals were drained and crystallised from light petroleum, and showed the normal density, melting point, boiling point, refractive index, and absence of rotatory power characteristic of cajeput oil. About 15 per cent. of the geraniol had been converted into terpineol.

Neither acetic acid nor acetic anhydride will convert geraniol into terpineol, but this change takes place rapidly on warming with acetic acid containing 1—2 per cent. of sulphuric acid, and more slowly, but with a better yield of terpineol, when the action takes place at the ordinary temperature.

For the separation of geraniol and terpineol, phthalic anhydride is used, which combines readily with the primary alcohols to form acid esters, but only slowly with secondary, and not at all with tertiary, alcohols; after neutralising the solution with soda, the unchanged terpineol can be extracted with ether, whilst sodium geranyl phthalate remains behind, and can be hydrolysed with caustic alkalis.

The conversion of geraniol into terpineol is explained by the formation of an additive product with two molecules of acid, which are subsequently split off with formation of a ring-compound; this intermediate product should be identical with that which is assumed to be formed in the conversion of linalool into terpineol, but it could not be isolated in either case.

By shaking with 5 per cent. sulphuric acid for 10 days and boiling the terpin hydrate formed with dilute sulphuric acid, geraniol can also be converted into a liquid terpineol identical with that prepared from pinene.

When steam is passed into an aqueous solution of sodium geranyl phthalate, there is produced, together with geraniol, a considerable amount of inactive linalool. This affords a third method of passing from geraniol to linalool (compare Tiemann, *Ber.*, 1898, 31, 832, and Schimmel's *Berichte*, April 1898, 25).  
T. M. L.

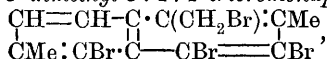
**Orientation in the Terpene Series: Exhaustive Bromination of Isogeraniolene and of Ionene.** By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1899, 32, 2429—2447. Compare *Abstr.*, 1898, i, 675).—It has been shown that when euterpene is submitted to the authors' process for converting monocyclic terpenes into the corresponding derivatives of benzene (*loc. cit.*), ethylxylene is produced, showing that bromination has not only removed hydrogen, but has also caused an atom of carbon to wander. Pursuing the line of inquiry suggested by this observation, the authors have obtained from isogeraniolene,  $\text{CMe}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CHMe} \\ \text{CH}_2 - \text{CH} \end{smallmatrix} \text{CH}$ , a mixture of the tetrabromides,  $\text{CMe} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{CH}_2\text{Br}) \\ \text{CBr} = \text{CBr} \end{smallmatrix} \text{CBr}$ , and  $\text{CMe} \begin{smallmatrix} \text{CBr} \cdot \text{C}(\text{CH}_2\text{Br}) \\ \text{CMe} - \text{CBr} \end{smallmatrix} \text{CBr}$ , whilst

ionene,  $\begin{array}{c} \text{CH}=\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{CH}_2 \\ \text{CMe}\cdot\text{CH}\cdot\text{CH}-\text{CH}\cdot\text{CH} \end{array}$ , yields the tetrabromide,  

$$\begin{array}{c} \text{CH}=\text{CH}-\text{C}\cdot\text{C}(\text{CH}_2\text{Br})\cdot\text{CMe} \\ \text{CMe}\cdot\text{CBr}\cdot\text{C}-\text{CBr}=\text{CBr} \end{array}$$

The mixture of tetrabromides, prepared by saturating with hydrogen bromide a solution of isogeraniolene in glacial acetic acid, pouring the liquid on ice, and treating the hydrobromide thus obtained with bromine (10 parts) and iodine (0.1 part), crystallised from ethylic acetate in long needles, and melted somewhat indefinitely at 137—139°; the mixture of acetyl derivatives, obtained by the action of silver acetate, crystallised from dilute acetic acid in needles and leaflets, and yielded a mixture of alcohols,  $\text{C}_9\text{H}_9\text{OBr}_3$ , which crystallised from ethylic acetate in long prisms and melted at 227—228.5°. Reduction with sodium amalgam removed bromine from the mixed alcohols, converting them into an oil, which chromic acid oxidised to the aldehydes; the latter reduced potassium permanganate, yielding paraxylic,  $\alpha$ -hemellithylic, and hemellitic acids. It follows that a methyl of the *gem*-dimethyl group in geraniolene has occupied one of the two possible ortho-positions, giving rise to hemellithene,  $\text{CMe}\langle\begin{array}{c} \text{CMe}\cdot\text{CMe} \\ \text{CH}=\text{CH} \end{array}\rangle\text{CH}$ , and pseudocumene.

1-Bromomethyl-2 : 3'-dimethyl-3 : 4 : 4'-tribromonaphthalene,



prepared from ionene hydrobromide and bromine with a small proportion of iodine, crystallises from xylene in flat prisms, and melts at 217—220°; when heated with nitrobenzene, glacial acetic acid, and silver acetate, it yields the *acetyl* derivative of 1-methylol-2 : 3'-dimethyltribromonaphthalene, which crystallises in long needles melting at 181—183°. 1-Methylol-2 : 3'-dimethyltribromonaphthalene,  $\text{C}_{13}\text{H}_{11}\text{OBr}_3$ , obtained on hydrolysing the acetyl derivative, melts at 230—231°; the *ethylic ether* crystallises from ethylic acetate, and melts at 141—142°. 1-Methylal-2 : 3'-dimethyltribromonaphthalene,  $\text{C}_{13}\text{H}_9\text{OBr}_3$ , formed on oxidising the alcohol with chromic acid, crystallises from benzene in needles and melts at 200—204°.

2 : 3'-Dimethyltribromo- $\alpha$ -naphthoic acid,  $\text{C}_{13}\text{H}_9\text{O}_2\text{Br}_3$ , prepared from the aldehyde by oxidation with nitric acid in nitrobenzene, melts at 244—245.5°; the *ethylic salt* crystallises in needles, and melts at 138—142°. 2 : 3'-Dimethyl- $\alpha$ -naphthoic acid,  $\text{C}_{13}\text{H}_{12}\text{O}_2$ , obtained on reducing the tribromo-derivative with sodium amalgam, crystallises from benzene in flat prisms, and melts at 168—171°. 2 : 3'-Dimethylnaphthalene,  $\text{C}_{12}\text{H}_{12}$ , formed on eliminating carbonic anhydride from the acid by means of hot lime, crystallises from alcohol in plates melting at 110—111°; the hydrocarbon is readily volatile in steam, and has a faint odour of orange-blossom. The *picrate* crystallises from alcohol in orange-yellow needles, and melts at 142—143°.

2 : 3'-Dimethyl- $\alpha$ -naphthaquinone,  $\text{C}_{12}\text{H}_{10}\text{O}_2$ , obtained by oxidising dimethyl- $\alpha$ -naphthoic acid with chromic acid, crystallises from ethylic acetate in yellow prisms, and melts at 137—138°; further oxidation with potassium permanganate converts the quinone into trimellitic acid.

1-Methylol-2:3'-dimethylnaphthalene,  $C_{13}H_{14}O$ , prepared from the acetyl derivative of the tribromo-compound by reduction with sodium amalgam, crystallises in long needles without a definite melting point; the *picrate* forms orange-yellow needles melting somewhat indefinitely at  $83^{\circ}$ . 1-Bromomethyl-2:3'-dimethylnaphthalene, obtained by the action of hydrobromic acid on the foregoing alcohol, crystallises in leaflets, and melts at  $107-108.5^{\circ}$ . Reduction with zinc dust and alcoholic hydrochloric acid converts it into 1:2:3'-trimethylnaphthalene,  $C_{13}H_{14}$ , which boils at  $154-156^{\circ}$  under 15 mm. pressure; the *picrate* melts at  $122-123^{\circ}$ . M. O. F.

**Ethereal Oils.** By SCHIMMEL AND Co. (*Chem. Centr.*, 1899, i, 1042-1043; from *Geschäftsber.*, April 1899).—Cananga oil, from Samarang in Java, is distilled from the green leaves and has practically the same physical constants as the other varieties of the oil. It is insoluble in 10 volumes of 95 per cent. alcohol, has a sp. gr. 0.930 at  $15^{\circ}$ , rotatory power  $-19^{\circ} 21'$ , and saponification number 24.34. The oil obtained from the yellow leaves has a sp. gr. 0.956 at  $15^{\circ}$ , rotatory power  $-25^{\circ} 11'$ , is insoluble in 10 volumes of 95 per cent. alcohol, and contains about 12 per cent. of eugenol. The odour of this oil is inferior to that of the Manilla oil.

Cognac oil has a sp. gr. 0.878-0.880 at  $15^{\circ}$ , rotatory power  $-0^{\circ} 3'-0^{\circ} 11'$ , acid number 50.9-68.6, ether number 140.9-218.6 and is soluble in two or more volumes of 80 per cent. alcohol. A higher sp. gr. or a higher ether number indicates the presence of artificial cognac oil.

The eucalyptus oil from *Eucalyptus macrorrhyncha*, which yields 0.287 per cent., is a reddish-brown liquid with a pleasant odour, has a sp. gr. 0.927 at  $18^{\circ}$  and contains 53.2 per cent. of cineol, traces of phellandrene, and considerable quantities of eudesmol (Baker and Smith, *Proc. Roy. Soc. New South Wales*, 1898, 32, 104). *Eucalyptus capitellata* yields 0.103 per cent. of a dark red oil which has a sp. gr. 0.9153 at  $18^{\circ}$  and contains 38.4 per cent. of cineol, traces of phellandrene, and a small quantity of eudesmol. *Eucalyptus eugenioides* yields 0.689-0.795 per cent. of a colourless oil with a pleasant odour; it has a sp. gr. 0.907-0.908 at  $22^{\circ}$ , specific rotatory power  $[\alpha]_D +3.745 +5.246^{\circ}$ , and contains 28.4-31.4 per cent. of cineol. *Eucalyptus dextropinea* yields 0.825-0.850 of an oil of sp. gr. 0.8743-0.8763 at  $17^{\circ}$  and *Eucalyptus laevopinea* 0.66 per cent. of an oil of sp. gr. 0.8732. The latter contains a large quantity of pinene (Baker, *Proc. R. Linn. Soc. New South Wales*, 26, 414), which has hitherto only been found in small quantities in oils of the globulus class. The authors do not approve of Baker's designation of the dextro- and lævo-pinenes obtained from these oils as eucalyptene and eudesmene respectively.

Heracleum oil, prepared by distilling the fruit of *Heracleum sphondylium*, contains octylic alcohol. Octaldehyde, obtained by oxidising the alcohol, boils at  $60-63^{\circ}$  under 10 mm. pressure, and has a sp. gr. 0.827 at  $15^{\circ}$ . By the action of  $\beta$ -naphthylamine and pyruvic acid on octylic alcohol, *octyl- $\beta$ -naphthacinchonic acid* is formed; it separates in white crystals and melts at  $234^{\circ}$ . By the action of phosphonium iodide on octylic alcohol, a compound which melts at  $115.5^{\circ}$  is obtained.

Jasmine oil contains benzylic acetate, linalylic acetate, and benzylic alcohol, but not phenylglycolmethyleneacetal. Jaborandi leaf oil contains an unsaturated hydrocarbon which melts at 28—29°.

Rosewood oil, obtained by distilling the wood of *Convolvulus scoparius*, has a sp. gr. 0.951 at 15°, rotatory power +1° 30', saponification number 0 and dissolves in 10 volumes of 95 per cent. alcohol. The saponification number of the acetyl derivative is 151.3.

From East Indian sandalwood oil, 85 per cent. of santalol may be isolated by means of phthalic anhydride. Santalol is a mixture of two sesquiterpene alcohols, of which the one of lower boiling point is inactive or dextrorotatory, whilst the other has a rotatory power -32° 36' and a sp. gr. 0.979 at 15°. Santalylphthalic acid could not be obtained in a crystalline form, but silver santalylphthalate melts at 50°.

The melting point of the nitrosochloride prepared from oil of thyme gives no indication of the presence or absence of pinene as Labbé supposes (this vol., i, 621), trustworthy evidence only being obtained by preparing derivatives of the chloride.

Vetiver oil contains palmitic acid.

The ethereal oil prepared from the roots of *Alpinia malaccensis*, which yields 25 per cent. is, according, to van Romburgh, a colourless oil which has a pleasant odour, a sp. gr. 1.039—1.047 at 27°, a rotatory power +0° 25' to +1° 5' (20 mm. tube) and solidifies on cooling with separation of methylic cinnamate.

E. W. W.

**Constituents of East Indian Sandalwood Oil.** By Hugo von SODEN and FR. MÜLLER (*Chem. Centr.*, 1899, i, 1082; from *Pharm. Zeit.*, 44, 258—269).—Sandalwood oil has been stated to consist mainly of santalol, a sesquiterpene alcohol,  $C_{15}H_{25} \cdot OH$ , boiling at above 300°. Santalol contains, however, at least two different alcohols, of which the one of lower boiling point is slightly laevorotatory or inactive whilst the other has a rotatory power of about -20° to -30°. The mixture boils at about 303—306°, and both alcohols have the same specific gravity. Heine and Co.'s gonorol is prepared from the mixture by hydrolysing and fractionating in a vacuum. A sesquiterpene, *santalene*,  $C_{15}H_{24}$ , prepared by hydrolysing and then fractionating the oil, is a thin, colourless oil which has the odour of cedar, boils at 261—262°, has a sp. gr. 0.898 at 15°, a rotatory power of about -21°, is soluble in 16 parts of 90 per cent. alcohol, and is easily so in chloroform, ether, benzene, or light petroleum. It combines with hydrogen chloride or bromide (2 mols.) to form volatile additive products, and when treated with glacial acetic acid or sulphuric acid and a small quantity of water, yields a liquid which is probably the sesquiterpene alcohol,  $C_{15}H_{26}O$ ; this has a strong, cedar-like odour, boils at 160—165° under 6 mm. pressure, and has a sp. gr. 0.978 at 15°.

Sandalwood oil also contains small quantities of phenols, lactones, and borneol (?). An acid which melts at about 154° was also isolated.

E. W. W.

**Isolauronic Acid: Constitution of Camphoric Acid, Camphor, and its Derivatives.** By G. BLANC (*Ann. Chim. Phys.*, 1899, [vi], 18, 181—288. Compare this vol., i, 630).—An exhaustive criticism of the formulæ for camphoric acid advocated by Brecht, Tiemann, and Bouveault leads the author to support that of the

last-named investigator; this expression,  $\text{CH}_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} \cdot \text{COOH} \\ \text{CH}_2 - \text{CH} \cdot \text{COOH} \end{smallmatrix}$ , although known as Bouveault's formula, was first suggested by W. H. Perkin, jun. (Proc., 1896, 12, 191), but has since been abandoned by that author in favour of the formula  $\begin{smallmatrix} \text{CH}_2 \cdot \text{CMe}_2 - \text{CMe} \cdot \text{COOH} \\ \text{CH}(\text{COOH}) \cdot \text{CH}_2 \end{smallmatrix}$  (Trans., 1898, 73, 796). Isolaauronic acid, or *trimethyl-1:1:2-cyclopentene- $\Delta^2$ -methyloic-3 acid*, has the formula  $\text{CMe}_2 \begin{smallmatrix} \text{CMe} \cdot \text{C} \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$ , whilst camphor is represented by the expression  $\text{CH}_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} \cdot \text{CO} \\ \text{CH}_2 - \text{CH} - \text{CH}_2 \end{smallmatrix}$ .

The paper deals with practical details relating to the preparation of isolaauronic acid and its derivatives; many of these compounds have been already described (Blanc, Abstr., 1897, i, 201, 538, and 554), but the following substances are mentioned for the first time.

*Isolaauronic aldehyde*,  $\text{C}_8\text{H}_{13} \cdot \text{CHO}$ , prepared by distilling a mixture of calcium isolauronolate and calcium formate, is a colourless, mobile liquid having an agreeable, penetrating odour; it boils at  $170^\circ$  under 760 mm. pressure, and its sp. gr. is 0.8930 at  $15^\circ$ . The aldehyde gives Schiff's reaction, and reduces ammoniacal silver nitrate; the compound with sodium hydrogen sulphite dissolves very freely in water. The *semicarbazone* melts and decomposes at  $212^\circ$ , and the *semioxamazone* at  $235^\circ$ . The *cinchonic acid*, prepared by heating the aldehyde with  $\beta$ -naphthylamine and pyruvic acid, crystallises in yellow leaflets and melts at  $257^\circ$ .

The *ammonium*, *strontium*, *magnesium*, *manganese*, and *cadmium* salts of isolaauronic acid are crystalline, and the *ferric* salt, which is insoluble in water and alcohol, crystallises from ether; the *amylic* salt, boiling at  $260^\circ$ , has a sp. gr. 0.9378 at  $15^\circ$ , and the *phenylic*,  *$\alpha$ -naphthylic*, and  *$\beta$ -naphthylic ethers* melt at  $24.5^\circ$ ,  $82^\circ$ , and  $82^\circ$  respectively. The *anhydride* is a viscous liquid which boils at  $210$ — $215^\circ$  under 13 mm. pressure, and has a sp. gr. 1.0287 at  $15^\circ$ . Both the *orthotoluidide* and *paratoluidide* melt at  $114^\circ$ , and the  *$\alpha$ -naphthalide* and  *$\beta$ -naphthalide* at  $148$ — $149^\circ$ .

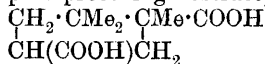
*Isolaauronic alcohol*,  $\text{C}_8\text{H}_{13} \cdot \text{CH}_2 \cdot \text{OH}$ , obtained on reducing the aldehyde or the chloride, has a camphor-like odour, boils at  $197^\circ$  under 760 mm. pressure, and has a sp. gr. 0.9023 at  $15^\circ$ ; the *acetyl* derivative boils at  $209$ — $210^\circ$ .

The *base*,  $\text{C}_8\text{H}_{13} \cdot \text{CHMe} \cdot \text{NH}_2$ , prepared by reducing isolaauronyl methyl ketoxime (Abstr., 1897, i, 554) with sodium in alcohol, boils at  $190^\circ$  under 760 mm. pressure, and has a sp. gr. 0.9558 at  $15^\circ$ ; the *hydrochloride* crystallises in small prisms which melt and decompose at  $230^\circ$ , and the *platinochloride* is an orange, crystalline powder. The *semicarbazone* of isolaauronyl methyl ketone melts and decomposes at  $232$ — $233^\circ$ ; on one occasion, a specimen melting at  $49^\circ$  was obtained (compare *loc. cit.*). M. O. F.

**Constitution of Camphoric Acid.** By G. BLANC (*Bull. Soc. Chim.*, 1899, [iii], 21, 830—854. Compare this vol., i, 536 and 630).

—The comparative merits of the formulæ  $\text{CH}_2 \begin{smallmatrix} \text{CMe}_2 \cdot \text{CMe} \cdot \text{COOH} \\ \text{CH}_2 - \text{CH} \cdot \text{COOH} \end{smallmatrix}$

(Bouveault, Blanc, compare preceding abstract) and



(Perkin, Trans., 1898, 73, 796), for camphoric acid are considered in the present paper.

The author approaches the discussion by way of isolauronolic acid, and recalls the following facts as having led him to adopt for this compound the constitutional formula  $\text{CMe}_2 \begin{array}{l} \text{CMe} \cdot \text{C} \cdot \text{COOH} \\ \text{CH}_2 - \text{CH}_2 \end{array}$ .

1. The acid is optically inactive. 2. Oxidation with nitric acid yields unsymmetrical *aa*-dimethylglutaric acid. 3. Oxidation with chromic acid yields dimethyl-3:3-hexanone-2-oic acid. 4. Isolaurelene,  $\text{C}_8\text{H}_{14}$ , obtained by heating isolauronolic acid in sealed tubes at  $300^\circ$ , also yields dimethylhexanonic acid when oxidised with potassium permanganate. 5. The ketone,  $\text{C}_8\text{H}_{18} \cdot \text{CO} \cdot \text{CH}_3$ , formed when acetic chloride acts on isolaurelene under the influence of aluminium chloride, is identical with the product of the action of zinc methyl on isolauronolic chloride.

It is next pointed out that the formula  $\text{CMe}_2 \begin{array}{l} \text{CHMe} \cdot \text{CH} \\ \text{CH}_2 - \text{C} \cdot \text{COOH} \end{array}$ , by which Perkin represents isolauronolic acid, is reached by ascribing the constitution  $\begin{array}{c} \text{CMe}_2 \cdot \text{CMe} \\ | \\ \text{CH}_2 - \text{C}(\text{COOH}) \end{array} \text{CO}$  to isolauronic acid, which he regards as the immediate product of oxidation, this formula being based on the assumption that dihydroiselauronic acid, the product of reduction with sodium amalgam, is an alcohol-acid which does not form a lactone. Repetition of his own experiments and a study of isolauronic acid, however, have led the author to results which confirm his previous conclusions, but are antagonistic to those of Perkin.

In the first place, purified isolauronolic acid is optically inactive. It is dimorphous, being obtainable in hexagonal prisms and large, slender plates belonging to the monoclinic system, and in octahedra belonging to the orthorhombic system, all three varieties melting at  $135^\circ$ . If the anhydride of racemic camphoric acid is employed for its production instead of dextrocamphoric anhydride, the product is the same, and cannot be resolved into optically active components by crystallising the cinchonine salt. Moreover, according to the author's view of the structure of isolauronolic acid, the compound obtained by Bürcker from the action of camphoric anhydride on benzene in presence of aluminium chloride (Abstr., 1895, i, 108; 1896, i, 179), should be optically active, and this is the case.

*Phenylidihydroiselauronolic acid*,  $\text{CMe}_2 \begin{array}{l} \text{CMePh} \cdot \text{CH} \cdot \text{COOH} \\ \text{CH}_2 - \text{CH}_2 \end{array}$ , crystallises in colourless needles from a mixture of alcohol and light petroleum, and melts at  $142^\circ$  (compare *loc. cit.*); a 5 per cent. solution in alcohol gives  $\alpha_D + 6^\circ 56'$  at  $20^\circ$ . The methylic salt melts at  $93-94^\circ$ , and gives  $\alpha_D + 11^\circ 53'$  at  $24^\circ$ , whilst the *isobutylic* salt melts at  $71-72^\circ$  and gives  $\alpha_D - 1^\circ 30'$  at  $23^\circ$ . The *chloride* crystallises in white needles melting at about  $60^\circ$ , and is very readily soluble in neutral solvents; moist air decomposes it, and when heated in a vacuum at about  $150^\circ$ ,



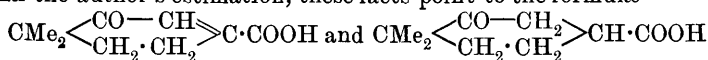
it is resolved into hydrogen chloride, carbonic oxide, and the unsaturated *hydrocarbon*  $C_{14}H_{18}$ , a somewhat viscous liquid which boils at  $195-200^{\circ}$  under 40 mm. pressure.

When isolauronic acid is oxidised with potassium permanganate at  $0^{\circ}$ , isolauronic acid is the main product, whilst oxalic, dimethylsuccinic, and dimethylhexanonic acids are formed in subordinate amount; if the operation is conducted at common temperatures, more than double the quantity of potassium permanganate is required, and the main products are oxalic and dimethylsuccinic acids, the amount of dimethylhexanonic and isolauronic acids being comparatively small. On oxidising the last-named substance with potassium permanganate at  $15-20^{\circ}$ , oxalic and dimethylsuccinic acids are produced, unaccompanied by a trace of dimethylhexanonic acid; according to Perkin (*loc. cit.*), this compound is formed when oxidation is effected by means of a mixture of chromic and sulphuric acids, but the quantity does not seem to be large. From these experiments, the author concludes that isolauronic acid is not the immediate result of oxidising isolauronic acid, but represents a stage subsequent to the formation of dimethylhexanonic acid.

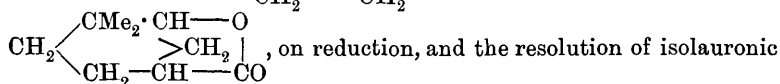
The final argument is based on the nature of dihydroisolauronic acid. As already stated, this compound is obtained on reducing isolauronic acid with sodium amalgam, and is regarded by Perkin as an

alcohol-acid,  $\begin{array}{c} CMe_2 \cdot CMe \\ | \\ CH_2 - C(COOH) \end{array} > CH \cdot OH$ , mainly on account of its inability to form a lactone. The author finds, however, that dihydroisolauronic acid is a ketone-acid, being not only indifferent towards acetic chloride, but capable of uniting with hydroxylamine and semicarbazide; the *oxime* and *semicarbazone* melt and decompose at  $210^{\circ}$  and  $229^{\circ}$  respectively. Dihydroisolauronic acid boils under the ordinary pressure without decomposition, and in consequence cannot have the ketonic group in the  $\beta$ -position with regard to carboxyl; it is therefore most probably a  $\gamma$ -ketone, and the  $\gamma$ -hydroxy-acid obtainable from it by reduction should be convertible into a lactone. This has been found to be the case. *Isolauronolide*,  $C_9H_{14}O_2$ , prepared by reducing dihydroisolauronic acid with sodium in absolute alcohol, has a faint odour of camphor, and melts at  $53-54^{\circ}$ ; hydrolysis converts it into *tetrahydroisolauronic acid*,  $C_9H_{16}O_3$ , which crystallises from benzene in small prisms and melts at  $142-143^{\circ}$ .

In the author's estimation, these facts point to the formulæ



for isolauronic and dihydroisolauronic acids respectively. The expressions accord with the conversion of the latter into tetrahydroisolauronic acid,  $CMe_2 \begin{array}{c} \text{CH(OH)} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH}_2 \end{array} > CH \cdot COOH$ , and isolauronolide,



on reduction, and the resolution of isolauronic acid into *aa*-dimethylsuccinic and dimethylhexanonic acids by oxidation. They are easily reconciled also with the production of aromatic acids

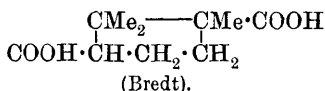
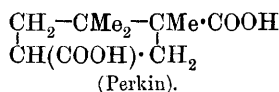
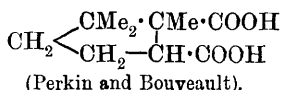
from isolauroic acid under the influence of concentrated sulphuric acid and fused caustic potash.

M. O. F.

**Perkin's Constitutional Formula for Camphoric Acid.** By G. BLANC (*Bull. Soc. Chim.*, 1899, [iii], 21, 854—863. Compare foregoing abstract).—Whilst admitting that Perkin's formula explains the production of dimethylmalonic, trimethylsuccinic and camphoric acids when camphoric acid is oxidised, the author points out that the formation of the acid  $C_8H_{12}O_5$  along with oxalic acid, observed by Balbiano, is incompatible with it (compare this vol., i, 537). Proceeding to deduce from Perkin's formula constitutional expressions for important members of the isolauroic and camphoric series, the author shows that conclusions to be drawn from this source are not easily reconciled with facts.

M. O. F.

**Constitution of Camphoric Acid. Synthesis of Ethylic Cyanodimethylcyclopentanone Carboxylate.** By WILLIAM A. NOYES (*Ber.*, 1899, 32, 2288—2292. Compare this vol., i, 284, 759).—Since the synthetical preparation of *i*-camphoric acid has shown the presence of the group  $\begin{array}{c} CMe_2 \cdot CMe \cdot C \\ | \quad \quad | \quad \quad | \\ C \quad \quad C \quad \quad C \end{array}$  in camphoric acid, the only formulæ containing a five-membered ring which are now admissible for this substance are those of



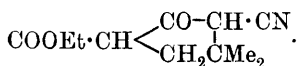
The second and third of these the author considers improbable from the fact that hydroxydihydrocampholytic acid does not yield a lactone when treated with dilute sulphuric acid, and therefore can hardly be a  $\gamma$ -hydroxy-acid, and that hydroxylauronic acid, not only does not yield a lactone, but on treatment with potassium dichromate and sulphuric acid loses carbonic anhydride and passes into a ketone, appearing therefore to be a  $\beta$ -hydroxy-acid. The second formula he considers inadmissible from the following facts.

[With J. W. SHEPHERD.]— *$\alpha$ -Hydroxydihydrociscampholytic acid*, obtained, in yield of about 10 per cent., when  *$\alpha$* -bromodihydrociscampholytic acid is heated with an aqueous solution of barium hydroxide at 30—40°, crystallises from light petroleum or benzene in needles melting at 112°; when boiled with lead dioxide and dilute sulphuric acid, it is transformed into a ketone,  $C_8H_{14}O$ , which boils at 167—169° and has a sp. gr. 0.8956 at 20°/4°. These figures, although uncertain, owing to the small quantities of substance, seem to point to this compound being a derivative of cyclopentanone. The oxime crystallises from alcohol in needles and melts at 104°.

If the second formula for camphoric acid were correct, this ketone should condense with 2 mols. of benzaldehyde, but it is found to

combine with 1 mol. only, yielding a *condensation product* which crystallises from alcohol in colourless needles and melts at  $74^{\circ}$ .

The authors hope to effect the synthesis of this ketone in the following way: ethylic sodiocyanacetate combines with ethylic  $\gamma$ -bromoisocaproate to form *ethylic cyanodimethylcyclopentanone carboxylate*, which crystallises from alcohol in needles melting at  $148.5^{\circ}$ , and according as alcohol is eliminated from one or other of the carbethoxy-groups, must have the constitution  $\text{CH}_2 \begin{matrix} \text{CO}-\text{C}(\text{CN})\cdot\text{COOEt} \\ \text{CH}_2\cdot\text{CMe}_2 \end{matrix}$  or



Ethylic  $\gamma$ -bromoisocaproate combines in a similar way with ethylic sodioacetoacetate to form a colourless oil boiling at  $180-190^{\circ}$  under 30 mm. pressure, and with ethylic sodiomethylmalonate to form an oil boiling at  $195-210^{\circ}$  under 30 mm. pressure; it is from the latter compound that it is hoped the 2:3:3-trimethylcyclopentanone, which is the constitution the author assigns to the ketone  $\text{C}_8\text{H}_{14}\text{O}$ , may be prepared.

The author considers that the formula  $\begin{matrix} \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{CMe}-\text{CMe}_2 \end{matrix}$  best expresses the constitution of camphor.

J. F. T.

The above formula for camphor has already been proposed by Bouveault (*Chem. Zeit.*, 1897, 21, 762).

J. F. T.

**Natural Resins** ["Überwallungsharze"]. IV. Larch Resin. By MAX BAMBERGER and ANTON LANDSIEDL (*Monatsh.*, 1899, 20, 647—659. Compare Abstr., 1898, i, 88).—Lariciresinol, after several recrystallisations from absolute alcohol and light petroleum or alcohol and water, forms white needles melting at  $169^{\circ}$ . It has the composition  $\text{C}_{17}\text{H}_{12}(\text{OMe})_2(\text{OH})_4$ , two of the hydroxyl groups being of a phenolic and two of an alcoholic character. The *tetracetyl* derivative crystallises from absolute alcohol in long needles, melts at  $160^{\circ}$ , and, on hydrolysis, yields a *substance*,  $\text{C}_{19}\text{H}_{22}\text{O}_6$  (isomeric with lariciresinol), crystallising from alcohol in plates which melt at  $97^{\circ}$ . When the potassium derivative of lariciresinol is boiled with acetic anhydride, a *triacyl* derivative is obtained; this crystallises from alcohol in white needles, melts at  $92^{\circ}$ , and, when hydrolysed, gives the same substance as the tetracetyl derivative.

*Diethylariciresinol*,  $\text{C}_{17}\text{H}_{12}(\text{OMe})_2(\text{OEt})_2(\text{OH})_2$ , is prepared by treating an alcoholic solution of lariciresinol with potassium hydroxide and ethylic iodide. It forms white needles melting at  $169^{\circ}$ , and is insoluble in dilute potassium hydroxide. The *dimethyl* derivative is obtained similarly in the form of white needles which very quickly agglomerate.

R. H. P.

**Resin of Convolvulus Althæoides.** By NICOLAS GEORGIADÈS (*J. Pharm.*, 1899, [vi], 10, 117—119).—The roots of *Convolvulus althæoides* contain about 7 per cent. of a greenish-yellow resin which is insoluble in water. The resin is rendered partially soluble in water by the action of cold sulphuric, hydrochloric, or nitric acids, but no coloration is produced. It is decomposed by dilute acids, and a soluble

reducing substance is formed. It is therefore probably composed of glucosides.

H. R. LE S.

**Essential Oils and Glucosides of Cresses.** By JOHANNES GADAMER (*Ber.*, 1899, 32, 2335—2341. Compare Abstr., 1898, ii, 180, and Hofmann, Abstr., 1874, 792—793).—When prepared by steam distillation from the finely cut plants, the essential oils of *Tropæolum majus* and of *Lepidium sativum* consist principally of benzylthiocarbimide; this is always mixed with benzylic cyanide, especially if the plants are only coarsely cut before the distillation. Both compounds are produced by the decomposition of a glucoside, the former by the action of the ferment myrosin, and the latter by the action of boiling water and acids. The glucoside could not be obtained in crystals, but when decomposed by silver nitrate gave an insoluble *silver* derivative, which dissolved at once in ammonia, separating again in a crystalline form with two molecules of ammonia; to this compound the formula  $\text{CH}_2\text{Ph}\cdot\text{N}:\text{C}(\text{SAg})\cdot\text{O}\cdot\text{SO}_3\text{Ag} + 2\text{NH}_3$  is assigned, and the acid from which it is derived is named '*tropæolic acid*'; the glucoside, to which the name of '*glucotropæolin*' is given, is regarded as having the constitution  $\text{CH}_2\text{Ph}\cdot\text{N}:\text{C}(\text{S}\cdot\text{C}_6\text{H}_{11}\text{O}_5)\cdot\text{O}\cdot\text{SO}_3\text{K} + 2\text{H}_2\text{O}$ .

The essential oil of *Nasturtium officinale* and *Barbarea præcox* consists chiefly of phenylethylenethiocarbimide,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}:\text{CS}$ , which was identified by converting it into the thiocarbamide; as in the previous case, Hofmann, using the coarsely cut plants, obtained only the corresponding nitrile. The glucoside from which these are derived is named '*gluconasturtiin*,' and is regarded as having the constitution  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}:\text{C}(\text{S}\cdot\text{C}_6\text{H}_{11}\text{O}_5)\cdot\text{O}\cdot\text{SO}_3\text{K} + x\text{H}_2\text{O}$ , but could only be obtained as a syrup; by decomposition with silver nitrate, it gives '*silver nasturtiate*,'  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{N}:\text{C}(\text{SAg})\cdot\text{O}\cdot\text{SO}_3\text{Ag} + 2\text{H}_2\text{O}$ , which also forms a crystalline compound with  $2\text{NH}_3$ , but loses this at ordinary temperatures.

When acted on by sodium thiosulphate, silver tropæolate and silver nasturtiate give a clear solution which probably contains the sodium salt, but soon decomposes into sodium sulphate and the thiocarbimide, which can then be extracted with ether.

T. M. L.

**Anemonin.** By HANS MEYER (*Monatsh.*, 1899, 20, 634—646. Compare Abstr., 1896, i, 623).—The hydroanemonin of Hanriot (*Bull. Soc. Chim.*, 1878, [ii], 47, 683) is shown to be a mixture of *anemonolic acid* and its *diethylic* salt. This mixture is formed when anemonin is reduced with zinc and alcoholic hydrochloric acid, and from it the acid is obtained after hydrolysis with dilute aqueous hydrochloric acid, *Anemonolic acid*,  $\text{C}_8\text{H}_{10}\text{O}_3(\text{COOH})_2 + \text{H}_2\text{O}$ , crystallises in the form of colourless tablets having a strong glassy lustre, and melts at 151—153°. It is dibasic, and forms soluble salts, with the exception of the *silver* salt, which is obtained as a bulky, white precipitate when silver nitrate is added to a neutralised solution of the acid. The *dimethylic* salt is formed when the silver salt is treated with methylic iodide, and also when anemonin dissolved in methylic alcohol is reduced by zinc and hydrochloric acid. It crystallises from ethylic acetate in large, lustrous tablets melting at 94—97°, and is very easily hydrolysed.

The paper concludes with a discussion of the formula of anemonin,

the author holding the view that this compound can form two classes of derivatives of the maleic and fumaric type. R. H. P.

**Reaction of Santonin and the Desmotroposantonins with Ferric Chloride.** By P. BERTOLO (*Gazzetta*, 1899, 29, ii, 102—103).—The violet coloration produced when santonin is heated with dilute sulphuric acid and ferric chloride is also obtained with the desmotroposantonins and the santonous acids. The author is of opinion that for this coloration to be formed, it is necessary that the santonin derivative should contain either a phenolic hydroxy-group, or a carbonyl group capable of being transformed into a phenolic hydroxy-group.

T. H. P.

**Resolution of Inactive Isosantonous Acid into its Dextro- and Lævo-components by means of Cinchonine.** By AMERIGO ANDREOCCI and P. ALESSANDRELLO (*Gazzetta*, 1899, 29, i, 479—483).—Isosantonous acid and cinchonine were dissolved in mol. proportions in 90 per cent. alcohol, and after adding a crystal of cinchonine dextrosantonate and allowing the liquid to evaporate, three crops of crystals and a syrupy residue were obtained. The first crystalline deposit was decomposed with dilute sulphuric acid and the liquid extracted with ether, the santonous acid thus obtained giving, after recrystallisation from alcohol, a specific rotatory power  $[\alpha]_D + 73^\circ$ , and after again crystallising from alcohol a melting point of  $178-179^\circ$ ; pure dextrosantonous acid has  $[\alpha]_D + 74.8^\circ$ , and a melting point of  $179-180^\circ$ . On treating the residual syrup in a similar manner, it is found to consist almost entirely of the cinchonine salt of the lævo-acid, since, after crystallising from alcohol, the acid obtained has  $[\alpha]_D - 74^\circ$ , and a melting point of  $179-180^\circ$ ; for pure lævo-santonous acid,  $[\alpha]_D - 74.4^\circ$ , and the melting point is  $179-180^\circ$ .

On partially saturating isosantonous acid with cinchonine, the proportions used being 2 mols. of the acid to 1 mol. of the base, a very good separation of the two isomerides is obtained, the salt of the dextro-acid separating first.

T. H. P.

**An Optically Active Partially Racemic Compound.** By AMERIGO ANDREOCCI (*Gazzetta*, 1899, 29, i, 513—516, and *Real. Accad. Linc.*, 1899, 8, 80—86).—From dextro- and lævo-acetyldesmotroposantonin, the former melting at  $156^\circ$  and having a specific rotatory power  $[\alpha]_D + 93.6^\circ$ , and the latter having a melting point  $154^\circ$  and an  $[\alpha]_D - 119^\circ$ , by fusing them together and repeatedly crystallising the product from alcohol, or by simple crystallisation alone, a lævo-rotatory acetyl derivative is obtained which melts at  $142^\circ$  and has a specific rotatory power  $[\alpha]_D - 12.8^\circ$ , which is the mean of those of the two components. Whilst the two components crystallise in slender prisms or needles, the double compound forms large, glistening prisms, and is much less soluble in acetic acid than its components. A dilute acetic acid solution of the double compound, when heated with a small quantity of sulphuric acid, gives rise to a mixture of the two desmotroposantonins, corresponding with the two original acetyl derivatives; from this mixture, the separate compounds are readily obtainable by crystallisation from alcohol or acetic acid.

T. H. P.

**Digitoxin and the Products of its Decomposition.** By HEINRICH KILIANI (*Arch. Pharm.*, 1899, 237, 446—454, and *Ber.*, 1899, 32, 2196—2201; the two papers are largely identical. Compare this vol., i, 70; and also Abstr., 1896, i, 59; 1897, i, 95).—When digitoxose,  $C_6H_{12}O_4$ , is oxidised with silver oxide and water, acetic acid is one of the products; hence digitoxose contains a CMe-group.

When digitoxigenin,  $C_{22}H_{32}O_4$ , is heated with 50 per cent. alcohol and sodium hydroxide at  $100^\circ$ , crystals of *sodium dixgenate*,  $C_{22}H_{33}O_5Na + H_2O$ , separate on cooling; the corresponding acid, *dixgenic acid*,  $C_{22}H_{34}O_5$ , melts at  $220$ — $230^\circ$ .

Under similar circumstances, digitoxin,  $C_{34}H_{54}O_{11}$ , yields *sodium digitoxate*; the crystalline *calcium salt*,  $(C_{34}H_{55}O_{12})_2Ca + 3H_2O$ , corresponding with this was analysed. The calcium salt does not yield digitoxin when treated with acetic acid. C. F. B.

**Digitalinum Verum and the Products of its Decomposition.** By HEINRICH KILIANI (*Arch. Pharm.*, 1899, 237, 455—458, and *Ber.*, 1899, 32, 2199; these are in part identical. Compare this vol., i, 71).—By oxidising digitaligenin with chromic acid in acetic acid solution, toxigenone is obtained, identical with that prepared in a similar manner from anhydroidigitoxigenin. C. F. B.

**Digitalein.** By HEINRICH KILIANI and ADOLF WINDAUS (*Arch. Pharm.*, 1899, 237, 458—466).—A digitalein in Schmiedeberg's sense (compare Abstr., 1892, 1482), that is, a substance which is readily soluble in water, and acts as a poison by paralysing the heart's action, can be obtained from *Digitalis* seeds. The mother liquor of the digitalin (Abstr., 1896, i, 52) is concentrated to a small bulk under diminished pressure, and the residue saturated with ether to prevent the growth of mould, and dialysed into water saturated with ether.

The dialysate is concentrated, extracted with ether to remove resin, and precipitated with 10 per cent. tannic acid in slight excess only. The precipitate is rubbed up with one-tenth of its weight of zinc oxide and some water, the mixture then evaporated, and the residue extracted with methylic alcohol. The ethereal extract is evaporated, and the residue extracted with water saturated with ether, when some digitalin remains undissolved. The extract is evaporated, the residue dissolved in alcohol (4 parts) and precipitated twice in succession with ether (2 parts), after which the alcohol-ether is evaporated to dryness. The residue of digitalein from 1 kilo. of *Dig. pur. pulv.* weighed 4—5 grams; a dose of 0.4 milligram produced permanent systole in the frog. C. F. B.

**Digitogenin and its Derivatives.** By HEINRICH KILIANI and ADOLF WINDAUS (*Arch. Pharm.*, 1899, 237, 466—471, and *Ber.*, 1899, 32, 2201—2205).—In consequence of Edinger's work (this vol., i, 377), digitogenin and some of its derivatives (compare Abstr., 1891, 577; 1895, i, 65) have been analysed afresh. The results do not render it possible to decide between  $C_{30}H_{48}O_6$ ,  $C_{30}H_{50}O_6$ , and  $C_{31}H_{52}O_6$  for the formula of digitogenin; that of digitogenic acid appears to be  $C_{28}H_{44}O_8$ ; a crystalline *cadmium salt*,  $C_{28}H_{42}O_8Cd + H_2O$ , of this acid was analysed.

When digitogenic acid is heated for a short time at  $160^\circ$ , it yields

two products, namely, digitoic acid (Abstr., 1893, i, 666) and an isomeride of itself. This substance,  $C_{28}H_{44}O_8$ , is named  *$\beta$ -digitogenic acid*; it differs from digitogenic acid in that it melts at  $105^\circ$ , and crystallises slowly from 50 per cent. alcohol in large, rather ill-defined prisms; like its isomeride, it is dibasic, and forms a crystalline magnesium salt and an oxime.

Oxydigitogenic acid,  $C_{28}H_{42}O_9$ , now appears to be tribasic, and not dibasic. C. F. B.

**A Compound of Glycuronic Acid with Parabromophenylhydrazine.** By CARL NEUBERG (*Ber.*, 1899, 32, 2395—2398).—If an aqueous solution of glycuronic acid is heated to boiling and treated with parabromophenylhydrazine acetate under certain conditions, a *compound* separates in bright, yellow needles, and may be purified by washing with water and absolute alcohol successively, and repeated crystallisation from 60 per cent. alcohol.

The new substance, whose exact nature has not yet been determined, has the composition,  $C_{12}H_{17}O_7N_2Br$ ; it is sparingly soluble in hot water, benzene, ether, ethylic acetate, absolute alcohol, or amyl alcohol, insoluble in chloroform, somewhat readily soluble in hot glacial acetic acid and in 60 per cent. alcohol. Its alcoholic solution is strongly dextrorotatory. It is scarcely altered by boiling with baryta water or ammonia, and does not give Bülow's reaction for acid hydrazides; the crystals, when moistened with alcohol, quickly reddened magenta sulphurous acid. The cupric-reducing power is diminished after treatment with 1 per cent. alcoholic hydrogen chloride, a behaviour which might indicate that acetal formation had occurred. It appears to combine with hydroxylamine, but an oxime could not be isolated, and it was not found possible to obtain derivatives containing more hydrazine, owing to the formation of resinous products.

The application of the above observation to the detection of glycuronic acid in urine is being investigated; it is to be noted that urochloralic acid yields the same compound after preliminary hydrolysis with dilute sulphuric acid. A. L.

**Plumieride.** By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 18, 334—350).—The plumieride isolated by Boorsma from the bark of *Plumiera acutifolia* appears to be identical with the substance obtained by Merck (Abstr., 1897, i, 167) from the same source, although the former investigator stated that it did not melt, whereas the latter gave its melting point as  $157$ — $158^\circ$ . The author finds that the substance melting at  $157^\circ$  is the hydrated form of plumieride; when crystallised from dry ethylic acetate, it separates in the anhydrous condition, and then has no definite melting point. A molecular weight determination by the cryoscopic method gave numbers varying from 537 to 572; these values are approximately half those obtained by Merck, who used the ebullioscopic method. Plumieride is a glucoside, for when boiled with 5 per cent. hydrochloric acid it is hydrolysed, yielding glucose and an insoluble, amorphous, brown substance. An acid, for which the author proposes the name *plumieridic acid*, is produced by dissolving plumieride in aqueous potash and allowing the solution to remain for some time; the solution, when acidified with

dilute sulphuric acid, yields the new compound, which is sparingly soluble in water. This acid is slightly soluble in methylic alcohol and insoluble in ethylic alcohol, ether, chloroform, or benzene; it decomposes at temperatures above  $200^{\circ}$ ; its dilute aqueous solution is lævoro-tatory. The potassium salt crystallises from water. Plumieridic acid is also a glucoside, for on boiling with 5 per cent. hydrochloric acid it behaves like plumieride, yielding glucose and an amorphous, brown substance. Plumieride seems also to be identical with agoniadin, obtained by Peckolt (*Arch. Pharm.*, 1870, ii, 142, 40) from *P. lancifolia*, for the latter substance behaves similarly on hydrolysis and melts at  $155^{\circ}$ . G. T. M.

**2:2':6:6'-Tetramethyldipyridyl and the Corresponding Tetracarboxylic Acid.** By FRANZ HUTH (*Ber.*, 1899, 32, 2209—2211. Compare Abstr., 1898, 687).—The gas evolved when 2:6-dimethylpyridine is heated with sodium consists of hydrogen and nitrogen, the former in larger amount.

The *hydrochloride*, *hydrobromide*, *hydriodide*, *nitrate*, and *silver nitrate* compound (with  $\text{AgNO}_3$ ) of the tetramethyldipyridyl are all unmelted at  $260$ — $280^{\circ}$ ; the nitrate crystallises with  $1\frac{1}{2}\text{H}_2\text{O}$ , and then melts at  $145^{\circ}$ .

The *calcium*, *barium*, and *copper* salts of the tetracarboxylic acid form insoluble precipitates; the first is crystalline in character. C. F. B.

**Picoline Haloids and Perhaloids.** By PAUL MURRELL (*J. Amer. Chem. Soc.*, 1899, 21, 828—854. Compare Prescott, Abstr., 1896, i, 316; Prescott and Trowbridge, *ibid.*, i, 186).— $\alpha$ -Picoline methiodide melts at  $224^{\circ}$ , Ramsay (Abstr., 1879, 263) gives the melting point as  $227^{\circ}$ . The corresponding  $\beta$ - and  $\gamma$ -compounds have not been obtained in a pure form, but their melting points are apparently much lower than that of the  $\alpha$ -compound.  $\alpha$ -Picoline ethiodide crystallises in colourless, feathery plates melting at  $123^{\circ}$  (compare Anderson, *Phil. Mag.*, 1855, [iv], 9, 214). *Picoline propiodide* crystallises from alcohol in yellowish needles melting at  $77^{\circ}$ ; the *isopropiodide* also crystallises in needles and melts at  $142^{\circ}$ ; the *butiodide* forms straw-coloured crystals melting at  $98^{\circ}$ ; the *isobutiodide* is a pale yellow syrup which does not solidify at  $-15^{\circ}$ ; the *secondary butiodide* is extremely unstable and could not be purified; picoline and tertiary butylic iodide, when heated at  $100^{\circ}$ , form picoline hydriodide and isobutylene. *Picoline isoamyl iodide* forms straw-coloured, cubical crystals melting at  $120^{\circ}$ , and *picoline allyliodide* transparent, almost colourless cubes melting at  $70^{\circ}$  (compare Ramsay, *loc. cit.*). Picoline hydriodide forms a snow-white mass which is somewhat unstable, readily decomposing into the base and hydrogen iodide. *Picoline hydrogen di-iodide*,  $\text{C}_6\text{H}_7\text{N}, \text{HI}, \text{I}$ , obtained by adding an alcoholic solution of iodine (1 equiv.) to an alcoholic solution of the hydriodide, forms dark brown prisms melting not very sharply at  $95^{\circ}$ . Like the other periodides, it is much more stable than the simple hydriodide, and, like them, it liquefies on contact with water. The *tri-iodide*,  $\text{C}_6\text{H}_7\text{N}, \text{HI}, \text{I}_2$ , forms dark brown octahedra melting at  $44^{\circ}$ ; the *pentiiodide*,  $\text{C}_6\text{H}_7\text{N}, \text{HI}, \text{I}_4$ , is obtained as a thick, greenish-black oil which does not solidify at  $-25^{\circ}$ .

$\alpha$ -Picoline methyl tri-iodide,  $\text{C}_6\text{H}_7\text{N}, \text{MeI}, \text{I}_2$ , forms bluish-black,



feathery plates melting at  $134^{\circ}$ , the isomeric  $\beta$ -compound melting at  $36^{\circ}$ , and the  $\gamma$ -compound at  $101^{\circ}$ .  $\alpha$ -Picoline methyl pentiodide,  $C_6H_7N, MeI, I_4$ , forms bluish-black needles melting at  $60^{\circ}$ , the  $\beta$ -compound is a brown-black oil which does not solidify at  $-25^{\circ}$ , and the  $\gamma$ -compound forms steel-blue needles melting at  $63^{\circ}$ . The  $\alpha$ -heptiodide forms dark-green, feathery plates melting at  $57^{\circ}$ ; and the  $\gamma$ -heptiodide dark-green, flat needles melting at  $81.5^{\circ}$ .  $\alpha$ -Picoline ethyl tri-iodide,  $C_6H_7N, EtI, I_2$ , is a dark brown oil and the pentiodide a green-black oil. Picoline propyl tri-iodide and pentiodide are also oils. Picoline isopropyl di-iodide,  $C_6H_7N, Pr^iI, I$ , forms light brown cubes melting at  $106^{\circ}$ , and the tri-iodide long, silky, light-brown needles melting at  $60^{\circ}$ , whereas the pentiodide is a greenish-black oil. Picoline butyl tri-iodide forms flat, light-brown needles melting at  $33^{\circ}$ . Picoline butyl pentiodide, picoline isobutyl tri-iodide, the corresponding pentiodide, picoline secondary butyl tri-iodide, and pentiodide are all oils. Picoline isoamyl di-iodide melts at  $96^{\circ}$ , the tri-iodide at  $22^{\circ}$ , whereas the pentiodide is an oil. Picoline allyl tri-iodide crystallises in purple-brown needles melting at  $62^{\circ}$ , but the pentiodide is an oil.

Picoline hydrochloride,  $C_6H_7N, HCl + \frac{1}{2}H_2O$ , melts at about  $200^{\circ}$  and the anhydrous salt at about  $80^{\circ}$ ; it is extremely deliquescent (compare Ramsay and also Anderson, *loc. cit.*).  $\alpha$ -Picoline methyl chloride is also extremely hygroscopic and melts not very sharply at about  $70^{\circ}$ ; the crystals contain  $1H_2O$ . Picoline methobromide forms long, colourless needles melting at  $217^{\circ}$ , picoline ethobromide melts at  $97^{\circ}$ , picoline hydrogen dibromide,  $C_6H_7N, HBr, Br$ , forms red rhombohedral crystals melting at  $76^{\circ}$ , the tribromide is a deep red oil. Ramsay (*loc. cit.*) describes a compound of the same composition melting at  $85^{\circ}$ .  $\alpha$ -Picoline methyl tribromide crystallises in orange-yellow plates melting at  $111^{\circ}$ ; picoline ethyl tribromide is a deep red oil. Picoline hydriodide bromide,  $C_6H_7N, HI, Br$ , obtained by mixing molecular proportions of picoline hydriodide and the hydriodide dibromide, forms dark-red crystals melting at  $68^{\circ}$ . Picoline hydriodide dibromide forms dark red crystals melting at  $58^{\circ}$ .  $\alpha$ -Picoline methiodide dibromide is best obtained by mixing the tribromide (2 mols.) with the tri-iodide (1 mol.) and crystallising from alcohol; it forms slender, orange-red needles, two or three inches long, melting at  $121.5^{\circ}$ .  $\alpha$ -Picoline methiodide iodobromide,  $C_6H_7N, MeI, IBr$ , crystallises in flat, interlaced needles of a reddish-brown colour melting at  $113^{\circ}$ . Picoline allyliodide dibromide crystallises in orange-yellow plates melting at  $84^{\circ}$ . The compounds described above are analogous to those of pyridine and with few exceptions agree with generalisations based on a study of the pyridine compounds (compare Prescott, *loc. cit.*). The normal iodides of picoline, as a rule, melt at a higher temperature than the corresponding pyridine iodides, and the same is more or less true of the periodides. In the case of complex perhaloids, the author thinks it probable that "it is the halogen of higher atomic weight that is next to the nitrogen" atom.

J. J. S.

**Action of Hydrogen Peroxide on Tertiary Bases.** By MARTIN AUERBACH and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 2507—2520. Compare Abstr., 1898, i, 536).—Propylpiperidine oxide,  $C_5H_{10} \cdot NPr^a \cdot O$ ,

obtained by allowing a mixture of propylpiperidine, acetone, and 5 per cent. hydrogen peroxide to remain for 2 weeks, forms a hygroscopic, crystalline mass, soluble in water, alcohol, or chloroform, but not in ether or light petroleum. Its halogen salts are extremely deliquescent, and the aurichloride is oily; the picrate is crystalline, and melts at 105°. In slightly acid solutions, it liberates iodine from potassium iodide. When heated with hydrochloric acid at 220° or with nitrous acid at 100°, the oxide is reconverted into propylpiperidine; when heated, it evolves propylene, whilst  $\delta$ -amidovaleraldehyde is left in the residue.

An additive product, 1-oxy-1-propylpiperidinesulphonic anhydride,  $C_3H_{10}NPr \begin{smallmatrix} \diagup O \\ \diagdown SO_2 \end{smallmatrix}$ , is produced by passing sulphurous anhydride into a solution of the oxide in water or chloroform; it melts at 131°, and is soluble in chloroform, acetone, benzene, water, or ether; when exposed to moisture, it is gradually converted into propylpiperidine sulphate.

*Isoamylpiperidine oxide* is less hygroscopic than the preceding oxide, and is prepared in a similar manner; its *hydrochloride* crystallises with  $1H_2O$ ; this is given off in the desiccator, and the dry salt melts at 102°; the hydriodide melts at 86°. Isoamylpiperidine forms an *aurichloride* melting at 128° and a *picrate* melting at 133°; its oxide forms an oily aurichloride and a *picrate* crystallising in needles and melting at 112°, and does not react with platinic chloride. Isoamylpiperidine oxide is reconverted into isoamylpiperidine by heating it alone or with hydrochloric or hydriodic acid; in the last case, the yield of tertiary base is quantitative. The *sulphonic anhydride* prepared by passing sulphurous anhydride into an aqueous solution of the oxide, separates in white crystals melting at 141°; in the presence of barium chloride, isoamylpiperidine hydrochloride and barium sulphate are produced. *Benzylpiperidine oxide*,  $C_3H_{10} \cdot N(CH_2Ph) \cdot O$ , crystallises from acetone and ether in lustrous, radiating needles containing  $\frac{1}{2}H_2O$ ; the *picrate* melts at 128°; the halogen salts are uncrystallisable, and the platinichloride is oily; the sulphonic anhydride melts at 131–132°. Hydrogen peroxide has no oxidising action on the acidylpiperidines; the presence of an acidic group seems to prevent the formation of a derivative of pentavalent nitrogen.

*Propionylpiperidine*, prepared by heating piperidine with ethylic propionate for 5 hours at 250°, is a liquid boiling at 230°, and very soluble in ether or water. *Isovaleryl piperidine* boils at 248° and is insoluble in water.

G. T. M.

**Stereochemistry of the Piperidine Series.** By W. HOHENEMSER and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 2520–2524).—The replacement of the imidic hydrogen of an optically active piperidine base by an alkyl radicle produces a marked increase in the specific rotation; for 2-methylpiperidine  $[\alpha]_D + 32^\circ$ , whilst for 2-methyl-1-ethylpiperidine it is  $+101.06^\circ$ ; on the other hand, the addition of the alkyl group to the side chain attached to the asymmetric carbon atom tends to diminish the optical activity, 2-propylpiperidine having a specific rotation of  $+15.7^\circ$ . The dextrorotatory forms of 1-ethyl-, 1-propyl-, and

1-isoamyl-pipecoline were obtained from the inactive bases by means of *d*-tartaric acid; their molecular rotations were +128·3, 141·4, and 150·1 respectively. The melting points of the following salts of 1-isoamyl- $\alpha$ -pipecoline are given:

Picrate	inactive	105°	active	-116°	active	+115°
Platinochloride	,,	130—135°	,,	187—188°	,,	181—182°
Hydrobromide	,,	deliquescent	,,	163°	,,	161° (indef.)
Hydrochloride	,,	,,	,,	155°	,,	150°
Mercurichloride	,,	oily	,,	oily	,,	oily.

1-*Isoamyl-2-pipecoline*, prepared by heating pipecoline with isoamyl bromide and solid potash for 16 hours at 125—130°, boils at 204—205° under 774 mm. pressure, and has a sp. gr. 0·8310 at 19°. G. T. M.

**Stereochemistry of the Piperidine Series.** By ARTHUR MARCUSE and RICHARD WOLFFENSTEIN (*Ber.*, 1899, 32, 2525—2531).—2:6-Dimethylpyridine (lutidine) was isolated from crude  $\beta$ -picoline by fractional distillation of the basic mixture and crystallisation of the picrate and hydrobromide; the latter salt is far less deliquescent than was formerly stated, it is stable on exposure to the atmosphere, and melts at 210°. On reduction with sodium and ethylic alcohol, 2:6-dimethylpyridine yields 2:6-dimethylpiperidine (lupetidine), and a new isomeride, *isolupetidine*; the two bases are separated by washing their hydrochlorides with acetone, when the isolupetidine salt passes into solution. The following salts of lupetidine were prepared: the *hydrobromide*, melting at 285°; the *acid tartrate*, melting at 79°, and the *picrate* at 162—164°. Lupetidine is inactive, and appears to be the meso-derivative, for it could not be separated into optically active forms by the tartrate method. Isolupetidine boils at 132—133° under standard pressure. The *hydrochloride* melts at 232—234°, the *hydrobromide* at 245°, the *picrate* at 124—127·5°, and the *thiocarbamate* at 124—125°; the bitartrate has not been obtained in a crystallised form.

G. T. M.

**Action of Phosphorus Tribromide on Isomeric Monatomic Saturated Alcohols.** Allylpiperidine. Allyldipropylamine. By NICOLAI A. MENSCHUTKIN (*Chem. Centr.*, 1899, i, 1066—1067; from *J. Russ. Chem. Soc.*, 1899, 31, 43—45).—By the action of phosphorus tribromide on ethylic, isobutylic, isopropylic, and tertiary amylic alcohol, large yields of the corresponding monobromides are obtained in a pure state, and the residue from the distillation consists of almost pure phosphorous acid.

When a mixture of solutions of piperidine and allylic bromide in benzene is heated on the water-bath, a theoretical yield of almost pure piperidine hydrobromide (which does not contain any diallylpiperidine ammonium hydrobromide) is obtained, and the filtrate, when fractionated, yields *allylpiperidine*. The latter boils at 151—152° and has a sp. gr. 0·8445 at 18·5°; the *aurichloride* forms a tough mass which is only soluble in hot water; the *platinochloride*,  $(C_3H_5 \cdot C_5NH_{10})_2 \cdot H_2PtCl_6$ , crystallises in dark orange prisms.

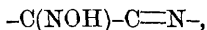
By the action of dipropylamine on allylic bromide dissolved in benzene, an almost theoretical yield of dipropylamine hydrobromide is obtained, and the solution yields *allyldipropylamine*, which boils at 150—152° and has a sp. gr. 0·7587 at 16°. The hydrochloride deliquesces

on exposure to the air, and by adding auric chloride to the solution the *aurichloride*,  $C_3H_5 \cdot NPr_2 \cdot HAuCl_4 + 2H_2O$ , melting at  $88-89^\circ$ , is formed with separation of gold. The *platinochloride*,  $(C_3H_5 \cdot NPr_2)_2 \cdot H_2PtCl_6 + H_2O$ , forms clear, orange crystals.

The preparation of these allyl compounds is not complicated by by-reactions as in the case of the action of methylic bromide on ammonia (compare Dübowsky, this vol., i, 854). E. W. W.

**Nitroso-indoles.** By ANGELO ANGELI and MATTEO SPICA (*Gazzetta*, 1899, 29, i, 500—503).—When treated with nitrous acid, indoles with substituent alkyl radicles in the 3'- or 2':3'-positions, give true nitrosamines, whilst if the alkyl group be in the 2'-position only, compounds are obtained which have been regarded as nitroso derivatives. Thus 2'-phenylindole yields a nitroso-2'-phenylindole, which is a yellow substance dissolving in alkali solutions with intense orange coloration, and readily yielding an acetyl derivative; it does not react with hydroxylamine. These properties are not in accord with those of the true nitroso-derivatives, which are coloured green or blue, and react with hydroxylamine, giving, in the case of aromatic derivatives, diazo-compounds, and in the case of the nitrosamines, the primitive amine with evolution of nitric oxide. From these considerations, the authors are of opinion that nitroso-2'-phenylindole is represented by the formula  $N \llcorner \begin{smallmatrix} C_6H_4 \\ CPh \end{smallmatrix} \gg C: NOH$ , corresponding with the ketone

$N \llcorner \begin{smallmatrix} C_6H_4 \\ CPh \end{smallmatrix} \gg CO$ . This formula, containing the grouping



bears out the analogy which these compounds show to the nitroso-phenols which contain the chain  $-C(NO\dot{H})-C \equiv C-$ . T. H. P.

**3'-Nitroso-indoles.** By MATTEO SPICA and F. ANGELICO (*Gazzetta*, 1899, 29, ii, 49—60).—The authors regard 3'-nitroso-indoles as containing the group NOH united to the carbon atom in the 3'-position of the indole nucleus. Such a constitution would indicate a method of preparation of these compounds by acting on the indole with amyl nitrite in presence of sodium ethoxide, and this method is now shown to give almost quantitative yields of nitroso-indoles identical with those obtained by means of nitrous acid in acid solution.

Isonitroso-2'-phenylindole gives an *acetyl* derivative,  $C_8H_4NPh:NOAc$ , crystallising from light petroleum in shining, red needles melting at  $121^\circ$ , and a *benzoyl* derivative, which separates from benzene in brilliant red needles, soluble in alcohol, and slightly so in light petroleum, and melting at  $151-152^\circ$  without decomposing.

*Isonitroso-2'-methylindole*,  $C_8H_4NMe:NOH$ , obtained from 2'-methylketole, separates from alcohol in brilliant, yellowish-green plates which change in the air and melt with decomposition at  $198^\circ$ ; acetic acid dissolves it, forming an intensely reddish-brown solution. It has both a basic and an acid character, yielding a potassium salt and a hydrochloride; with benzaldehyde, it gives no condensation product, showing that the indole character is lost. Its stability towards permanganate in alcoholic solution points to the absence of a double linking between

two carbon atoms. The *potassium* salt,  $C_9H_7ON_2K$ , forms orange-yellow, acicular crystals which, in the air, rapidly absorb moisture and carbonic anhydride and decompose.

*Isonitroso-2'-methylindole hydrochloride* forms an olive-green, crystalline mass which readily loses hydrogen chloride in the air, and is soluble in water with partial decomposition.

*Isonitrosopyrroline*,  $C_4H_5N:NOH$ , obtained by the action of amyl nitrite on pyrroline in presence of sodium ethoxide, is a yellowish-brown precipitate which rapidly blackens in the air. Its *sodium* derivative forms orange-coloured crystals. T. H. P.

**Constitution and Reactions of "Isatoic Acid."** By ERNST ERDMANN (*Ber.*, 1899, 32, 2159—2172).—Kolbe's isatoic acid (*Abstr.*, 1885, 58) has, according to E. von Meyer, the constitution

$C_6H_4 \begin{smallmatrix} \text{N} \cdot \text{COOH} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{O} \end{smallmatrix}$ , whereas Niementowski and Rozanski (*Abstr.*, 1889,

996) represent it by the formula  $C_6H_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{O} \end{smallmatrix}$ . The author brings forward the following reasons for supporting the second constitution: 1. Methylic chlorocarbonate reacts with anthranilic acid in the same manner as the ethylic salt, yielding phenylurethancarboxylic acid melting at  $181^\circ$ , and this is identical with the product formed by the action of methylic alcohol on "isatoic acid." 2. Phenylurethancarboxylic acid, when etherified with methylic alcohol, yields a neutral etheric salt melting at  $61^\circ$ , which is also obtained when methylic chlorocarbonate reacts with methylic anthranilate. 3. "Isatoic acid" is most readily obtained by the action of carbonyl chloride on an aqueous solution of sodium anthranilate. "Isatoic acid" is thus not an acid, but the anhydride of a dicarboxylic acid,  $\text{COOH} \cdot C_6H_4 \cdot \text{NH} \cdot \text{COOH}$ . The author calls this dibasic acid isatoic acid, and the anhydride, previously known as isatoic acid he terms *isatoic anhydride*. The formation of the anhydride by the action of ethylic chlorocarbonate on anthranil at  $140^\circ$  is easy to understand if the old formula,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix}$ , for anthranil is accepted and the formation of an additive product,  $\text{COCl} \cdot C_6H_4 \cdot \text{NH} \cdot \text{COOEt}$ , assumed, as this, by loss of ethylic chloride, would give isatoic anhydride.

A yield of some 50 per cent. of the anhydride is obtained by Niementowski and Rozański's method, provided an excess of ethylic chlorocarbonate is employed and the mixture is boiled long enough. The simplest method is, however, to pass carbonyl chloride into an aqueous solution of sodium anthranilate, and to crystallise the precipitated anhydride from alcohol; it is thus obtained in the form of glistening prisms; it crystallises from its aqueous solutions in colourless needles; the temperature at which it decomposes appears to vary greatly ( $240$ — $290^\circ$ ), according to the medium from which it crystallises. The anhydride has no acid reaction towards moist litmus paper, and dissolves but slowly in cold sodium carbonate solution, and may be precipitated unchanged on the addition of acids. Prolonged contact, however, with sodium carbonate decomposes it into carbonic anhydride and anthranilic acid, together with an acid,  $C_{15}H_{12}O_5N_2$ , probably

*diphenylcarbamidedicarboxylic acid*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOH})_2$ . A better yield of this acid is obtained when hot sodium carbonate solution is employed; it crystallises from dilute alcohol, melts and decomposes at  $165^\circ$ , has a strongly acid reaction, is readily soluble in alcohol, and only very sparingly in water; when heated with lime, it yields diphenylamine and aniline. Its *sodium* salt,  $\text{C}_{15}\text{H}_{10}\text{O}_5\text{N}_2\text{Na}_2 + \text{H}_2\text{O}$ , forms colourless, crystalline crusts, and is readily soluble in water.

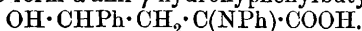
When isatoic anhydride is heated with methylic alcohol at  $130^\circ$  (compare Schmidt and Meyer, Abstr., 1888, 371), the chief product is *methylic hydrogen isatoate* (phenylurethancarboxylate),  $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COOMe}$ , which crystallises from dilute alcohol in colourless needles melting at  $181^\circ$ ; it is identical with the product formed by the action of methylic chlorocarbonate on anthranilic acid, and also with the compound described by Schmidt as methylic carb-oxyanthranilate. In addition to the acid etheric salt described above, an oily bye-product containing anthranilic acid, methylic anthranilate, and dimethylic isatoate is also formed. It has been found impossible to convert the acid etheric salt into methylic anthranilate, either by heating with methylic alcohol or with glycerol (compare Schmidt, *loc. cit.*); with the latter reagent, a small quantity of a volatile syrupy base has been obtained, but its constitution has not been determined.

*Dimethylic isatoate*,  $\text{COOMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COOMe}$ , is best obtained by boiling equal quantities of methylic chlorocarbonate and methylic anthranilate for an hour; it may also be obtained by further etherifying the acid etheric salt; it crystallises in glistening, white needles melting at  $61^\circ$ , is readily soluble in alcohol, but only sparingly in benzene, and is readily volatile in steam.

J. J. S.

**Formation of 2'-Alkylquinoline-4'-carboxylic Acid.** By KARL GARZAROLLI-THURNLACKH (*Ber.*, 1899, 32, 2274—2277).—Doebner (Abstr., 1887, 504; 1888, 300) first prepared 2'-phenylquinoline-4'-carboxylic acid by the interaction of aniline, benzaldehyde, and pyruvic acid in benzene solution at  $100^\circ$ ; at the same time, a neutral substance,  $\text{C}_{22}\text{H}_{18}\text{ON}_2$ , was also formed, which had previously been obtained by him from the same condensation in ethereal solution at the ordinary temperature.

The author considered that in this reaction either (I) the benzylideneaniline formed by the condensation of benzaldehyde with aniline combined with pyruvic acid to form  $\alpha$ -keto- $\gamma$ -anilidophenylbutyric acid,  $\text{NHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$ , or (II) the benzylideneaniline combined with pyruvic acid to form  $\text{NPh}\cdot\text{CMe}\cdot\text{COOH}$  and benzaldehyde, which again condensed to form  $\alpha$ -anil- $\gamma$ -hydroxyphenylbutyric acid,



In the first case, by the elimination of water, 2'-phenyldihydroquinoline-4'-carboxylic acid would be produced, which by the elimination of 2 atoms of hydrogen and rearrangement would be transformed into 2'-phenylquinoline-4'-carboxylic acid; in the second case, by a similar process, 4'-phenylquinoline-2'-carboxylic acid would be formed.

In order to settle this point, molecular quantities of benzylideneaniline and pyruvic acid were warmed together in alcoholic solution, when Doebner's neutral substance,  $\text{C}_{22}\text{H}_{18}\text{ON}_2$ , separated, and from the

mother liquors 2'-phenylquinoline-4'-carboxylic acid was obtained, and showed complete identity with Doebner's acid.

It is evident that Doebner and von Miller's quinaldine synthesis can be explained in the same way. J. F. T.

**5-Chloro-1-phenyl-3-methylpyrazole.** By AUGUST MICHAELIS and R. PASTERNAK (*Ber.*, 1899, **32**, 2398—2412).—This oily substance, obtained by heating 1-phenyl-3:4-dimethyl-5-pyrazolone with phosphorus oxychloride (this vol., i, 233), is not a chlorophenyldimethylpyrazole, as was at first supposed, but 5-chloro-1-phenyl-3-methylpyrazole,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CCl}:\text{CH} \end{smallmatrix}$ . It is formed by the elimination of methylic chloride

from the methochloride of chlorophenylmethylpyrazole produced in the first stage of the reaction. It is most easily obtained by heating 1-phenyl-3-methyl-5-pyrazole with phosphorus oxychloride, and forms a thick, colourless liquid with a characteristic odour, and boils unaltered at 261° under ordinary pressures, at 148° under 20 mm., and at 134° under 10 mm. pressure; it has a sp. gr. 1.1999 at 18°. It is a feeble base and dissolves in fairly concentrated sulphuric acid, but is reprecipitated by much water. The *hydrochloride*,  $\text{C}_{10}\text{H}_9\text{N}_2\text{Cl}\cdot\text{HCl}$ , produced by leading hydrogen chloride into an ethereal solution of the base, is very hygroscopic, decomposes on exposure to the air, and melts at 87—88°. The *platinochloride*,  $(\text{C}_{10}\text{H}_9\text{N}_2\text{Cl})_2\cdot\text{H}_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ , forms broad leaflets, loses water at 100°, and melts at 174°.

**5-Chloro-1-phenyl-3-methylpyrazole methochloride**,  $\text{NPh} \begin{smallmatrix} \text{NMeCl}:\text{CMe} \\ \text{CCl}=\text{CH} \end{smallmatrix}$ , is formed when antipyrine is heated with phosphorus oxychloride at 150°; it forms large, transparent crystals containing  $1\text{H}_2\text{O}$ , which become moist on exposure to the air, and effloresce on exposure in a vacuum over sulphuric acid; it dissolves readily in water, alcohol, or chloroform, but is insoluble in ether; the hydrated crystals fuse at 116—117°, but the anhydrous substance melts at 224°, and at higher temperatures breaks up into methylic chloride and chlorophenylmethylpyrazole. The aqueous solution gives precipitates with phosphotungstic and phosphomolybdic acids, potassium mercuric iodide, potassium, cadmium, or bismuth iodide, platinic and auric chlorides, and with bromine water. The *platinochloride*,  $(\text{C}_{10}\text{H}_9\text{N}_2\text{MeCl})_2\cdot\text{PtCl}_6$ , crystallises from hot water in yellowish-brown leaflets melting at 218°. The *aurichloride*,  $(\text{C}_{10}\text{H}_9\text{N}_2\text{MeCl})_2\cdot\text{AuCl}_4$ , forms light yellow leaflets and melts at 145°. The *mercurichloride*,  $\text{C}_{10}\text{H}_9\text{N}_2\text{Cl}\cdot\text{MeCl}\cdot\text{HgCl}_2$ , forms compact, transparent crystals which melt indefinitely at 98°.

By heating the methochloride with a 10 per cent. solution of sodium hydroxide, antipyrine is formed.

The *methobromide*,  $\text{NPh} \begin{smallmatrix} \text{NMeBr}:\text{CMe} \\ \text{CCl}=\text{CH} \end{smallmatrix}$ , crystallises from a mixture of absolute alcohol and ether in long, white needles, and melts at 256°. A *perbromide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{ClBr}_3$ , is obtained on adding bromine to a solution of the methochloride in glacial acetic acid; it crystallises from hot alcohol in yellow leaflets and melts at 136°, and when boiled with water yields the foregoing methobromide.

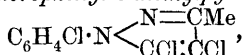
The *methiodide*,  $\text{NPh} \begin{smallmatrix} \text{NMeI} \cdot \text{CMe} \\ | \\ \text{CCI} = \text{CH} \end{smallmatrix}$ , forms long, colourless needles, is sparingly soluble in cold water, but dissolves readily in hot water, and is insoluble in ether. A *periodide*,  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{ClH}_2\text{I}_4$ , is formed when a solution of iodine in potassium iodide is added to an aqueous solution of the methochloride; it crystallises from hot water in dark, iodine-like leaflets having a green surface colour, dissolves very sparingly in water, but is readily soluble in hot alcohol and glacial acetic acid, and readily parts with iodine.

5-Iodo-1-phenyl-3-methylpyrazole *ethiodide*,  $\text{NPh} \begin{smallmatrix} \text{NEtI} \cdot \text{CMe} \\ | \\ \text{CI} = \text{CH} \end{smallmatrix}$ , produced when the chloropyrazole is heated with excess of ethylic iodide for 6 hours at  $100^\circ$ , forms long, white needles, is nearly insoluble in cold water, but dissolves readily in boiling water and hot alcohol, and melts and decomposes at  $240^\circ$ . When it is heated with moist silver chloride, the *ethochloride*,  $\text{C}_{10}\text{H}_9\text{N}_2\text{I} \cdot \text{EtCl}$ , is formed; this melts and decomposes at  $222^\circ$ , yielding ethylic chloride and 5-iodo-1-phenyl-3-methylpyrazole as a brownish liquid.

When chlorophenylmethylpyrazole, dissolved in light petroleum, is warmed with excess of bromine, a *perbromide*,  $\text{C}_{10}\text{H}_8\text{N}_2\text{ClBr}_3$ , is obtained. This forms a yellow, unstable powder which cannot be purified by recrystallisation, and readily loses 2 atoms of bromine. It dissolves in hot alcohol, decomposing slightly, and melts at  $99^\circ$ . When it is heated with sodium hydroxide until all colour is removed, it yields 5-chloro-4-bromo-1-phenyl-3-methylpyrazole,  $\text{NPh} \begin{smallmatrix} \text{N} = \text{CMe} \\ | \\ \text{CCI} \cdot \text{CBr} \end{smallmatrix}$ , a substance which crystallises in slender, silky, white needles, is soluble in strong hydrochloric acid, and melts at  $56^\circ$ .

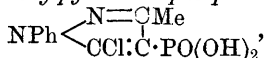
4:5-Dichloro-1-phenyl-3-methylpyrazole,  $\text{NPh} \begin{smallmatrix} \text{N} = \text{CMe} \\ | \\ \text{CCI} \cdot \text{CCI} \end{smallmatrix}$ , may be prepared by the direct chlorination of the corresponding monochloro-compound with chlorine or phosphorus pentachloride; it crystallises from alcohol in white needles, and melts at  $155^\circ$ . When heated at  $100$ — $120^\circ$  with methylic iodide, it yields 5-chloro-1-phenyl-3-methyl-4-iodopyrazole *methiodide*,  $\text{NPh} \begin{smallmatrix} \text{NMeI} \cdot \text{CMe} \\ | \\ \text{CMe} = \text{CI} \end{smallmatrix}$ , which separates from hot water in long, white needles, and melts and decomposes at  $229^\circ$ .

4:5-Dichloro-1-parachlorophenyl-3-methylpyrazole,



is formed when chlorine is passed into the monochloropyrazole for a long time; it crystallises from hot alcohol in white needles melting at  $130^\circ$ , is sparingly soluble in cold alcohol, but readily in the hot liquid, and dissolves in strong hydrochloric acid.

5-Chloro-1-phenyl-3-methylpyrazole-4-phosphinic acid,



is formed in small quantity when phosphorus oxychloride acts on antipyrine and the product is treated with water; it may also be ob-



tained in a similar manner from chlorophenylmethylpyrazole or its methochloride; it separates from hot water in compact, white leaflets which melt at  $191^{\circ}$ , is sparingly soluble in ether or cold water, but is somewhat readily dissolved by hot water or alcohol. The *silver* salt,  $C_{10}H_8N_2Cl \cdot PO(OAg)_2$ , is a white, amorphous powder insoluble in water, but readily dissolved by aqueous ammonia. The phosphinic acid is completely decomposed, when heated alone or with strong hydrochloric acid at  $150^{\circ}$ , into metaphosphoric acid and chlorophenylmethylpyrazole. A. L.

**Some Amido- $\alpha$ -phenylbenzimidazole Derivatives.** By OTTO KYM (*Ber.*, 1899, 32, 2178—2180. Compare this vol., i, 647, for analogous benzoxazoles).—Benzodinitranilide and 2'-phenyl-2-amido-benzimidazole (Muttelet, this vol., i, 500) can be obtained, the first by heating 1 : 2 : 4-dinitraniline with benzoic chloride at  $160$ — $180^{\circ}$ , the second by reducing this first product with stannous chloride and hydrochloric acid; the *acetyl* derivative of the second substance melts at  $245$ — $246^{\circ}$  when dry. The pale yellow *paranitrobenzodinitranilide*,  $C_6H_3(NO_2)_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$ , melting at  $195$ — $196^{\circ}$ , can be obtained in a similar manner, and reduced to *paramido-2'-phenyl-2-amidobenzimidazole*,  $NH_2 \cdot C_6H_3 \langle \begin{smallmatrix} NH \\ N \end{smallmatrix} \rangle C \cdot C_6H_4 \cdot NH_2$ ; this melts at  $235$ — $236^{\circ}$  when dry; its *acetyl* derivative melts above  $305^{\circ}$ . C. F. B.

**Oxidation of Alkylhalides of Benzimidazoles.** By JOHANNES PINNOW and CARL SÄMANN (*Ber.*, 1899, 32, 2181—2191).—2 : 1' : 2'-*Trimethylbenzimidazole methochloride*,  $C_6H_3Me \langle \begin{smallmatrix} NMe \\ NMeCl \end{smallmatrix} \rangle CMe$ , is obtained from the corresponding methiodide (Niementowski, *Abstr.*, 1887, 937) by treating this with lead acetate and hydrochloric acid in succession. Potassium permanganate oxidises it at  $90$ — $95^{\circ}$  to *phenylenedimethylcarbamide-carboxylic* (1' : 3'-*dimethylbenzimidazolone-2-carboxylic*) acid,  $COOH \cdot C_6H_3 \langle \begin{smallmatrix} NMe \\ NMe \end{smallmatrix} \rangle CO$ ; this melts at  $281$ — $282^{\circ}$ ; its *calcium* and *lead* salts crystallise each with  $3H_2O$ ; when nitrated, it yields a *dinitrophenylenedimethylcarbamide*,  $C_6H_2(NO_2)_2 \langle \begin{smallmatrix} NMe \\ NMe \end{smallmatrix} \rangle CO$ , which remains unmelted at  $270^{\circ}$ . In the oxidation mentioned above, some *tolylenedimethylcarbamide* (2 : 1' : 3'-*trimethylbenzimidazolone*),  $C_6H_3Me \langle \begin{smallmatrix} NMe \\ NMe \end{smallmatrix} \rangle CO$ , is formed also. The carboxylic acid described is also formed when the methochloride of 2 : 1'-dimethylbenzimidazole (*Abstr.*, 1898, i, 182) is oxidised with permanganate at  $55$ — $100^{\circ}$ ; this *methochloride* melts at  $228$ — $229^{\circ}$ , and crystallises with  $1H_2O$ ; the *methiodide* was analysed also. Trimethylbenzimidazole *ethobromide*, which is formed much less readily than the methiodide and melts at  $236$ — $237^{\circ}$ , behaves like its methyl analogue when oxidised with permanganate at  $48$ — $65^{\circ}$ , but gives a far worse yield; 1'-methyl-3'-ethylbenzimidazolone-2-carboxylic acid melts at  $233$ — $234^{\circ}$ .

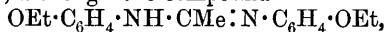
1 : 2-Dimethylbenzimidazole (phenylenemethylethenylamidine) *methochloride*,  $C_6H_4 \langle \begin{smallmatrix} NMe \\ NMeCl \end{smallmatrix} \rangle CMe$ , is obtained from the corresponding

methiodide (O. Fischer, Abstr., 1892, 1475); it melts at 225—230°, and crystallises with 2H<sub>2</sub>O; when oxidised with permanganate at the ordinary temperature, at 47—52°, and at 57—64° in succession, it yields *phenylenedimethylcarbamide*,  $C_6H_4 \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} \text{CO}$ , which melts at 108.5—110°. This substance is also formed when the sodium salt of phenylenemethylcarbamide is heated at 103—106° with methylic iodide in methyl alcoholic solution. *Phenylenemethylcarbamide*,  $C_6H_4 \begin{smallmatrix} \text{NMe} \\ \text{NH} \end{smallmatrix} \text{CO}$ , is obtained by heating orthonitraniline hydrobromide with methylic alcohol at 100°, reducing the methylnitraniline formed to amidomethylaniline, and condensing this with carbonyl chloride in benzene-toluene solution; it melts at 191—192°. 1':2'-Dimethylbenzimidazole methochloride is converted by sodium methoxide, or by caustic potash on heating, into 1':2':3'-*trimethylbenzimidazolinol*,  $C_6H_4 \begin{smallmatrix} \text{NMe} \\ \text{NMe} \end{smallmatrix} \text{CMe} \cdot \text{OH}$ ; this melts at 164—165°.

C. F. B.

**Orthamidophenetidine.** By GEORG COHN (*Ber.*, 1899, 32, 2239—2243).—The following experiments were undertaken with the object of ascertaining the effect of various constitutional changes on the physiological effect of a compound. 3-Ethoxybenzimidazolone,  $\text{OEt} \cdot C_6H_3 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{CO}$ , is prepared by the action of phosgene on orthamidophenetidine, and crystallises in lustrous, white plates melting at 266—268°. The compound has not a sweet taste, although it is closely related in constitution to dulcine,  $\text{OEt} \cdot C_6H_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ .

3-Ethoxyphenylene-ethenyldiamine, 3-ethoxy-2'-methylbenzimidazole,  $\text{OEt} \cdot C_6H_3 \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{CMe}$ , is best obtained by the action of acetic anhydride and sodium acetate on amidophenetidine, and forms a white, crystalline powder melting at 149—150°. The *hydrochloride* is a white, soluble powder which has a bitter taste. This compound is not an anæsthetic, although the compound



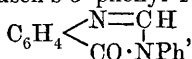
with which it is closely related, has anæsthetic properties.

Ethoxymethylbenzimidazole is accompanied by *diacetylamidophenetidine*, which melts at 188°, and by a blue colouring matter. Methylic iodide converts it into 3-ethoxy-1':2'-dimethylbenzimidazole *hydriodide*,  $\text{OEt} \cdot C_6H_3 \begin{smallmatrix} \text{NMe} \\ \text{N} \end{smallmatrix} \text{CMe} \cdot \text{HI}$ , which crystallises in fascicular groups of long needles; the *base* forms slender needles melting at 102°. 3-Ethoxy-2'-isobutyrylbenzimidazole,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{C} \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C}_6H_3 \cdot \text{OEt}$ , obtained by the action of isovaleric acid on the benzimidazole, melts at 135—136°.

A. H.

**Preparation of 3'-Phenyldihydroquinazoline (Orexine).** By VICTOR KULISCH (*Chem. Centr.*, 1899, i, 847; from *Zeit. Österr. Apoth.-V.*, 37, 138—141).—Quinazoline and its homologues containing alkyl groups in the miazine ring may be prepared by the condensation of

orthamidobenzaldehyde with formamide, or an amide of a higher acid. By heating orthamidobenzoic acid (1 mol.) with formanilide (1 mol.) at 123—130° for an hour, a compound is obtained which is identical with Paal and Busch's 3'-phenyl-4-ketoquinazoline,



prepared by oxidising orexine with potassium permanganate (Abstr., 1890, 72). This compound crystallises from ether in slightly yellow, rhombic crystals, and when reduced in alkaline solution with tin and hydrochloric acid, yields the dihydro-compound, orexine,  $\text{C}_{14}\text{H}_{12}\text{N}_2$ , which crystallises in small, lustrous plates and melts at 94—96°.

E. W. W.

**Benzoflavines.** By RICHARD E. MEYER and RUDOLF GROSS (*Ber.*, 1899, 32, 2352—2371).—Oehler's "Benzoflavine, 6B.F.O.," consists principally of the hydrochloride of a *diamidodimethylphenylacridine*,

$\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{CPh} \end{array} > \text{C}_6\text{H}_2\text{Me} \cdot \text{NH}_2$ , which can be isolated by dissolv-

ing the dye in dilute acetic acid and precipitating with caustic soda; the base crystallises from alcohol in brownish-yellow, stunted prisms, and yields a *hydrochloride*,  $\text{C}_{21}\text{H}_{19}\text{N}_3$ ,  $2\text{HCl} + \text{H}_2\text{O}$ , crystallising in brownish-red needles, a *hydriodide*,  $\text{C}_{21}\text{H}_{19}\text{N}_3 \cdot \text{HI}$ , which forms brownish-yellow, elongated plates, a *hydrobromide*,  $\text{C}_{21}\text{H}_{19}\text{N}_3 \cdot \text{HBr}$ , crystallising from alcohol in rhombic pyramids and from acetic acid in long, brownish-red needles, and a *sulphate*, which separates in long, red prisms; all these salts dissolve in alcohol with a green fluorescence.

When benzaldehyde is added to an alcoholic solution of equivalent quantities of 1:2:4-tolylenediamine and its hydrochloride at 60°, *tetramidoditolylphenylmethane hydrochloride*,  $\text{C}_{21}\text{H}_{24}\text{N}_4$ ,  $4\text{HCl} + 2\text{H}_2\text{O}$ , is precipitated in the form of bright yellow plates; the *base*,  $\text{CHPh}[\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2]_2$ , crystallises from chloroform in beautiful, rhombic plates and melts at 230—231°. *Benzylidenemetatolylenediamine*,  $\text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2$ , the intermediate product of this action, can be prepared by adding benzaldehyde to 1:2:4-tolylenediamine suspended in water; it forms large, yellow plates, melts at 90—91°, is easily hydrolysed by dilute acids at the ordinary temperature, and, when warmed with metatolylenediamine hydrochloride in alcoholic solution for 3 hours at 60—70°, is converted into tetramidoditolylphenylmethane hydrochloride. When the latter is heated with dilute hydrochloric acid of sp. gr. 1·07 for 7 hours at 160°, ammonia is eliminated, and a mass of red needles of the hydrochloride

of *diamidodihydrophenylacridine*,  $\text{CHPh} \begin{array}{c} \diagup \text{C}_6\text{H}_3(\text{NH}_2) \\ \diagdown \text{C}_6\text{H}_3(\text{NH}_2) \end{array} > \text{NH}$ , formed; this, however, cannot be isolated, owing to the ease with which it is oxidised by the air, to form the benzoflavine hydrochloride described above; the formation of the latter is accelerated by adding ferric chloride.

Attempts to diazotise "benzoflavine, 6B.F.O.," by the usual methods, using sodium or amyl nitrite, failed, but by passing nitrous acid fumes into a solution of the base in concentrated sulphuric acid and subsequently adding the diazo-solution obtained to boiling alcohol,

the two amido-groups were eliminated, and  $\mu$ -phenyl-2:7-dimethyl-acridine,  $\begin{array}{c} \text{CH}=\text{CH}-\text{C}\cdot\text{N}-\text{C}\cdot\text{CH}:\text{CH} \\ | \quad | \quad | \quad | \\ \text{CMe}:\text{CH}\cdot\text{C}\cdot\text{CPh}\cdot\text{C}\cdot\text{CH}:\text{CMe} \end{array}$ , formed; this crystallises from

alcohol, chloroform, or benzene in needles, from light petroleum in light yellow, rhombic plates, melts at 166—167°, and dissolves in acids with a green fluorescence. The *hydrochloride*,  $\text{C}_{21}\text{H}_{17}\text{N}\cdot\text{HCl}$ , and the *hydrobromide* form bright yellow plates, the *hydriodide* crystallises in fan-shaped aggregates, the *sulphate*,  $\text{C}_{21}\text{H}_{17}\text{N}\cdot\text{H}_2\text{SO}_4$ , in prisms, and the *methiodide*,  $\text{C}_{21}\text{H}_{17}\text{N}\cdot\text{MeI}$ , in long, red needles which melt at 186—187°. The structure of the base follows from its being formed on heating paratolylamine with benzoic acid and zinc chloride for 10 hours at 260°; from this, taking into account recent views as to the structure of fluorescein, the authors attribute to "benzoflavine, 6B.F.O.," the constitution  $\begin{array}{c} \text{NH}_2\cdot\text{C}:\text{CH}\cdot\text{C}\cdot\text{N}-\text{C}\cdot\text{CH}:\text{C}\cdot\text{NH}_2 \\ | \quad | \quad | \quad | \\ \text{Me}:\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{CPh}\cdot\text{C}\cdot\text{CH}:\text{CMe} \end{array}$ , although two other formulæ are possible.

An attempt to decide between these by eliminating the carboxyl group of the compound  $\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}_3$ , obtained by the action of ammonia on fluorescein (Meyer and Oppelt, Abstr., 1891, 246), which has since been shown to be a diamidophenylacridinecarboxylic acid,  $\begin{array}{c} \text{NH}_2\cdot\text{C}:\text{CH}\cdot\text{C}\cdot\text{N}-\text{C}\cdot\text{CH}:\text{C}\cdot\text{NH}_2 \\ | \quad | \quad | \quad | \\ \text{CH}:\text{CH}\cdot\text{C}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{COOH})\cdot\text{C}\cdot\text{CH}:\text{CH} \end{array}$  (German Patents, 1893, 73334 and 75933), led to no issue; moreover, the *diamidophenylacridine*,  $\begin{array}{c} \text{NH}_2\cdot\text{C}:\text{CH}\cdot\text{C}\cdot\text{N}-\text{C}\cdot\text{CH}:\text{C}\cdot\text{NH}_2 \\ | \quad | \quad | \quad | \\ \text{CH}:\text{CH}\cdot\text{C}\cdot\text{CPh}\cdot\text{C}\cdot\text{CH}:\text{CH} \end{array}$ , which should have been the pro-

duct of this action, could not be obtained in a pure state by the interaction of benzaldehyde with metaphenylenediamine. The interaction of these substances in molecular proportion yields *dibenzylidenemetaphenylenediamine*,  $\text{C}_6\text{H}_4(\text{N}:\text{CHPh})_2$ , which crystallises from ether in aggregates of yellow needles and melts at 104—105°.

The authors confirm the statements contained in the German patents cited above with reference to the fluorescein derivative,  $\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}_3$ ; the ethylic salt,  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_3\text{Et}$ , prepared according to these patents, crystallises from 50 per cent. alcohol in needles or plates, melts at 247—248°, and forms a crystalline *hydrochloride*,  $\text{C}_{20}\text{H}_{14}\text{O}_2\text{N}_3\text{Et}\cdot 2\text{HCl}$ .  
W. A. D.

**Oxy-compounds of Pyrrodiazole.** By AMERIGO ANDREOCCI and V. MANNINO (*Gazzetta*, 1899, 29, ii, 41—48. Compare Abstr., 1898, i, 277).—By means of phosphorus pentachloride, derivatives of urazole and of 3- and 5-pyrrodiazolone are reduced to pyrrodiazole compounds, and pyrazolones similarly yield pyrrazoles. In the case of phenyl-urazole and paratolylurazole, however, Pellizzari and Ferro (this vol., i, 550) have shown that by moderating the action of the phosphorus pentasulphide, intermediate compounds consisting of phenyl- and tolyl-derivatives of 3-thiotriazolone and of 3-thiobistriazole are obtained. With a view to discovering the mechanism of the reducing action of the pentasulphide, the authors have attempted to reduce these thio-compounds to pyrrodiazole derivatives by means of hydrogen sulphide or ammonium sulphide, but negative results were obtained.

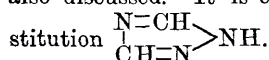
That the reducing action is not due to hydrogen phosphides is shown by the failure of the reaction of these phosphides with 1-phenyl-3-methyl-5-pyrroldiazolone to yield a reduction product; with the same compound, neither phosphorous acid nor ordinary phosphorus gave a definite product.

The action of phosphorus oxychloride on phenylpyrroldiazolone gives rise only to the formation of phosphorus compounds, but if the trichloride be present, phenylpyrroldiazole is obtained.

It is concluded that in the reduction of pyrroldiazolones by chlorine or sulphur compounds of phosphorus, the reducing action is not exerted directly on the pyrroldiazolone, but on intermediate chloro- or thio-derivatives.

T. H. P.

**Relation of 2:4-Pyrroldiazole to Benzene and to Cyclic Compounds of the Pyridine and Pyrroline Types.** By AMERIGO ANDREOCCI (*Gazzetta*, 1899, 29, ii, 1—22).—A detailed account is given of the synthetical processes which give rise to 2:4-pyrroldiazole and its derivatives, the general behaviour of the pyrroldiazole group and its analogies to benzene, pyrroline, 2-pyrazole, and pyridine being also discussed. It is concluded that 2:4-pyrroldiazole has the con-



T. H. P.

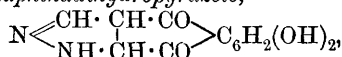
**Condensation of Diazomethane with Quinones.** By HANS VON PECHMANN and EUGEN SEEL (*Ber.*, 1899, 32, 2292—2300).—The first product of the action of diazomethane on quinone in ethereal solution is a white, unstable diazo-compound which soon becomes yellow, and when drained becomes brownish-red on exposure to air and generally explodes as soon as it is dry. If allowed to remain under the ether for one or two days, or, better, if mixed with one-third the volume of alcohol, cooled to 0° for one hour and extracted with dilute caustic soda, the diazo-compound passes into a stable isomeride, *diketobenzobisdihydropyrazole*,  $\text{N} \begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \\ | \\ \text{NH} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{NH} \end{array} \text{N}$

or  $\text{N} \begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{CH} \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \end{array} \text{N}$ , which separates on acidifying the alkaline solution with dilute sulphuric acid. It is a colourless powder, which begins to blacken at 280° and decomposes at 300°; is insoluble in the ordinary solvents, dissolves in caustic soda to a yellow solution from which strong alkali precipitates the yellow *sodium* derivative, and dissolves in sodium carbonate solution on boiling. It is not acted on by oxidising or reducing agents, but the insoluble *silver* derivative is acted on by methylic iodide and gives a product insoluble in alkalis. The *diacetyl* compound crystallises from a mixture of acetic acid and acetic anhydride in colourless or feebly-yellowish needles, becomes brown above 300°, does not dissolve in the ordinary solvents, but is at once hydrolysed by dilute alkalis. The *diphenylhydrazone* melts at 266°, crystallises from a mixture of acetone and benzene as a yellow, microcrystalline powder, is only slightly soluble in most solvents, but gives a blue solution in concentrated sulphuric acid, whilst the solution

in acetic acid gives a red coloration and then a reddish-brown precipitate with ferric chloride.

*Diketonaphthadihydropyrazole*,  $N \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CO} \\ | \\ \text{NH} \cdot \text{CH} \cdot \text{CO} \end{smallmatrix} > C_6H_4$ , prepared by the action of diazomethane on  $\alpha$ -naphthoquinone, crystallises from glacial acetic acid in colourless needles, sublimes on heating, chars at  $280^\circ$ , dissolves only very slightly in ordinary solvents, but more readily in pyridine, dissolves in caustic alkalis to a greenish-yellow solution, and in sodium carbonate solution on boiling. The silver derivative, when treated with methylic iodide, gives a methylic derivative insoluble in alkalis; oxidising and reducing agents are without action on it; bromine in chloroform solution gives a red, crystalline *additive product* which loses its bromine on exposure to air. The *monobenzoyl* derivative crystallises from much alcohol in felted needles, melts at  $185^\circ$ , and dissolves readily in chloroform. The *monophenylhydrazone* crystallises from acetic acid in felted, brick-red needles, melts with decomposition at  $272^\circ$ , is sparingly soluble in most solvents, but dissolves in concentrated sulphuric acid to a violet solution, and in alcoholic potash to a green solution which becomes brown on adding water. The *monoxime* melts at  $276^\circ$ , crystallises from acetic acid or pyridine in needles, and dissolves in caustic alkalis to a yellow solution.

*Dihydroxydiketonaphthadihydropyrazole*,



prepared by hydrolysis of the acetyl compounds, forms slender, orange-red needles, melts at  $300^\circ$ , is slightly soluble in the ordinary solvents, giving solutions which show a yellowish-green fluorescence; it dissolves in concentrated sulphuric acid to a red solution with brownish-yellow fluorescence, and in alkalis to a magenta-red solution. The *diacetyl* derivative, prepared by the action of diazomethane on diacetylnaphthazarine, melts at  $175^\circ$ , crystallises from acetone in needles, is only slightly soluble in most solvents, more readily in pyridine or boiling acetic acid, and dissolves in alkalis to a violet solution, from which acids liberate the dihydroxy-compound as a red, flocculent precipitate. The *triacetyl* derivative crystallises from glacial acetic acid in greenish flakes, melts at  $173^\circ$  to an orange-coloured fluid, dissolves only very slightly in ordinary solvents, most readily in pyridine, gives a magenta-red solution in concentrated sulphuric acid, and is readily hydrolysed by acids or alkalis.

*Pyrazole-4:5-dicarboxylic acid*,  $N \begin{smallmatrix} \text{CH} \cdot \text{C} \cdot \text{COOH} \\ | \\ \text{NH} \cdot \text{C} \cdot \text{COOH} \end{smallmatrix}$ , prepared by

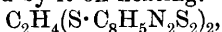
oxidising the above triacetate with nitric acid, crystallises in white, glistening, efflorescent needles, with  $1H_2O$ , melts at  $260^\circ$  with evolution of gas, and dissolves readily in alcohol or water; its constitution is shown by its preparation from methylic 4:5-pyrazolinedicarboxylate (Pechmann, Abstr., 1894, i, 438) by oxidation with nitric acid. The *methylic* salt, prepared by oxidising methylic 4:5-pyrazolinedicarboxylate with bromine, crystallises from hot water in white, felted needles, dissolves in most solvents, and melts at  $141^\circ$ .

On heating above the melting point, pyrazole-4 : 5-dicarboxylic acid loses carbonic anhydride and yields pyrazole. T. M. L.

**Diazole Group. III. Phenylthiodiazolonethiol.** By MAX BUSCH and W. STRAMER (*J. pr. Chem.*, 1899, [ii], 60, 187—191. Compare this vol., i, 825).—The *ethylic ether* of phenylthiodiazolonethiol,

$\text{NPh} \begin{array}{c} \text{N}=\text{C} \cdot \text{SEt} \\ | \\ \text{CS} \cdot \text{S} \end{array}$ , prepared by the action of ethylic iodide on the

potassium derivative, crystallises from alcohol in large, silvery flakes, and melts at 66°. It forms an *iodine additive product*,  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{I}_2\text{S}_3$ , which dissolves readily in hot benzene, and crystallises, on cooling, in splendid, dark-red prisms, melts at 123°, and is decomposed by bisulphite solution. The corresponding *bromide* melts at 131°, crystallises from benzene in magnificent orange-red, silky needles, and does not dissolve in cold alcohol, but is decomposed by it on heating. The *ethylenic ether*,

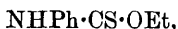


forms stout, transparent crystals, melts at 145°, dissolves readily in boiling benzene or chloroform, and slightly in alcohol, ether, or ethylic acetate. The *benzylic ether*,  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2 \cdot \text{S} \cdot \text{CH}_2\text{Ph}$ , separates from alcohol in stout, yellowish crystals, and melts at 93°. The *benzoyl* derivative,  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2 \cdot \text{SBz}$ , melts at 154°, crystallises from a mixture of chloroform and alcohol in glistening, white needles, and dissolves readily in boiling benzene or chloroform, but only slightly in other solvents.

When reduced with sodium amalgam, the thiol yields phenylthiodiazolinethiol,  $\text{NPh} \begin{array}{c} \text{N}=\text{C} \cdot \text{SH} \\ | \\ \text{CH}_2 \cdot \text{S} \end{array}$  (Abstr., 1896, i, 190). Diazobenzene

chloride interacts with the potassium salt of the thiol to form the *diazosulphide*,  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2 \cdot \text{S} \cdot \text{N}_2\text{Ph}$ , an unstable, yellow precipitate readily soluble in ether, benzene, or alcohol.

Phenylthiodiazolone bisulphide, when acted on with alcoholic potash, re-forms the thiol, but the sulphinic acid,  $\text{NPh} \begin{array}{c} \text{N}=\text{C} \cdot \text{SO}_2\text{H} \\ | \\ \text{CS} \cdot \text{S} \end{array}$ , which should also be produced, appears to be hydrolysed to phenylthiodiazolone,  $\text{NPh} \begin{array}{c} \text{N}=\text{CH} \\ | \\ \text{CS} \cdot \text{S} \end{array}$ , and then to phenylthiourethane,



which forms the chief product of the action.

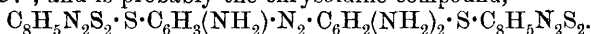
T. M. L.

**Diazole Group. IV. Action of Amines on Phenylthiodiazolone Bisulphide.** By MAX BUSCH and JAS. WOLFF (*J. pr. Chem.*, 1899, [ii], 60, 192—196. Compare Abstr., 1896, i, 705).—The chief products of the action of orthophenylenediamine on phenylthiodiazolone bisulphide are the *orthophenylenediamine* salt of phenylthiodiazolonethiol, which forms long, rose-coloured needles, and melts at 180°, and *phenylthiodiazolonethiol orthodiamidophenylic ether*,  $\text{NPh} \begin{array}{c} \text{N}=\text{C} \cdot \text{S} \cdot \text{C}_6\text{H}_3(\text{NH}_2)_2 \\ | \\ \text{CS} \cdot \text{S} \end{array}$  [ $\text{NH}_2 : \text{NH}_2 : \text{S} = 1 : 2 : 4$ ]; this separates

from benzene in stout crystals, dissolves in hot alcohol or chloroform, and melts at 159—160°. The constitution of this base is shown by the formation of an *azimido*-compound  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2 \cdot \text{S} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{N}$ ,

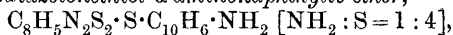
by the action of nitrous acid; it crystallises from alcohol or acetic acid in slender needles, melts at 186—187°, and possesses feeble acid properties.

The *metadiamidophenylic ether* of phenyldithiodiazolonethiol crystallises from dilute alcohol in bunches of stout needles. *Phenyldithiodiazolonethiol metadiamidophenylic ether* [ $\text{NH}_2 : \text{NH}_2 : \text{S} \cdot \text{C}_8\text{H}_5\text{N}_2\text{S}_2 = 1 : 3 : 5$ ], melts at 164—165°, crystallises from alcohol in colourless needles, dissolves slightly in ether or benzene and readily in chloroform, and shows a green fluorescence in alcoholic solution. The action of nitrous acid on the base gives a brownish-red precipitate, which separates from alcohol, acetic acid, or benzene in minute crystals, melts at 156—157°, and is probably the chrysoidine compound,



Paraphenylenediamine does not appear to act on the disulphide.

*Phenyldithiodiazolonethiol  $\alpha$ -aminonaphthyllic ether*,



melts at 132—133°, crystallises from alcohol in bunches of white needles, dissolves in the ordinary solvents on heating, and very readily in acetone. The *hydrochloride* forms colourless needles, and when acted on with nitrous acid gives a bordeaux-red solution of the *diazo*-compound, which combines with  $\beta$ -naphthol to a bordeaux-red *azo-dye*, which crystallises from acetic acid or benzene in slender needles, melts at 221—222°, and gives a blue-violet solution in concentrated sulphuric acid.

*Phenyldithiodiazolonethiol  $\beta$ -aminonaphthyllic ether*, [ $\text{NH}_2 : \text{S} = 2 : 1$ ], forms colourless, silky needles, melts at 152°, and dissolves fairly readily in the ordinary solvents on heating. The *hydrochloride* forms pale yellow tablets. The *diazo*-compound combines with  $\beta$ -naphthol to form an *azo-dye*, which crystallises in beautiful, vermilion-red needles, and melts at 199—200°.

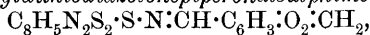
Unlike ethylaniline, diphenylamine does not act on the bisulphide.

T. M. L.

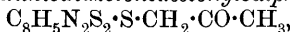
**Diazole Group. V. Condensation of Phenyldithiodiazolone-hydrosulphamine with Aldehydes and Ketones.** By MAX BUSCH and JOS. WOLFF (*J. pr. Chem.*, 1899, [ii], 60, 197—205. Compare Abstr., 1896, i, 705).—In alcoholic solution, formaldehyde reduces the hydrosulphamine,  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2 \cdot \text{S} \cdot \text{NH}_2$ , to the bisulphide,  $\text{S}_2(\text{C}_8\text{H}_5\text{N}_2\text{S}_2)_2$ , and ammonia, but does not form an ald.sulphime; in aqueous solution, a viscous and partially resinous product is obtained. Similarly, acetaldehyde and cenanthaldehyde give only oily products. Furfuraldehyde, like benzaldehyde, gives a sulphime, *phenyldithiobiazolonefurfuralsulphime*,  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2 \cdot \text{S} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_4\text{OH}_3$ , which melts at 152°, crystallises from a mixture of alcohol and chloroform in colourless needles, crystallises well from benzene, and dissolves slightly in alcohol or ether. When treated with alcoholic hydrogen chloride in dry ethereal solution, the sulphime is converted into *furfuraldime hydrochloride*,  $\text{C}_4\text{OH}_3 \cdot \text{CH} \cdot \text{NH} \cdot \text{HCl}$ , which crystallises in colourless, feathery needles, softens at 50°, and melts at 52° to a turbid, yellow oil; water decomposes it into furfuraldehyde and ammonium chloride, whilst phenylhydrazine gives furfuralphenylhydr-



azine and ammonium chloride. *Phenyldithiodiazolonemetanitrobenzalsulphime*,  $C_8H_5N_2S_2 \cdot S \cdot N : CH \cdot C_6H_4 \cdot NO_2$ , forms microscopic needles, melts at  $173-174^\circ$  to a yellow oil, decomposes at  $200^\circ$  with frothing to a red liquid, and dissolves readily in chloroform and benzene. *Metanitrobenzaldime hydrochloride*,  $NO_2 \cdot C_6H_4 \cdot CH : NH, HCl$ , forms minute, colourless needles, melts at  $249-250^\circ$  to a reddish-yellow oil, and gives metanitrobenzaldehyde when acted on by water. *Phenyldithiodiazoloneanisalsulphime*,  $C_8H_5N_2S_2 \cdot S \cdot N : CH \cdot C_6H_4 \cdot OMe$ , melts at  $145-146^\circ$ , and crystallises from a mixture of chloroform and alcohol in colourless needles. *Anisaldime hydrochloride*,  $OMe \cdot C_6H_4 \cdot CH : NH, HCl$ , forms minute, colourless needles, softens at  $170^\circ$ , and melts at  $175-176^\circ$ . *Phenyldithiodiazolonepiperonalsulphime*,



crystallises from a mixture of chloroform and alcohol in minute needles, from benzene in silky, colourless needles, and melts and decomposes at  $183-184^\circ$  to a reddish-brown oil. *Piperonaldime hydrochloride*,  $CH \cdot O_2 \cdot C_6H_3 \cdot CH : NH, HCl$ , crystallises from benzene in minute, colourless needles, softens at  $180^\circ$ , and melts at about  $229-230^\circ$  to a dark-coloured oil. Acetone does not give the ketosulphime, but a partial reduction occurs, with separation of ammonia, and two other substances are formed; the *substance*, to which the formula  $C_8H_5N_2S_2 \cdot S \cdot NH \cdot CMe_2 \cdot S \cdot C_8H_5N_2S_2$  is assigned, is only very slightly soluble in the ordinary solvents but more readily in boiling xylene, acetic acid, amyl alcohol, or chloroform; it crystallises from the latter in small, transparent, glistening prisms, melts and decomposes at  $186-187^\circ$  to a brown liquid, shows a normal molecular weight in naphthalene solution by the cryoscopic method, is not decomposed by boiling hydrochloric acid or caustic soda, but gives phenyldithiodiazolonebisulphide when warmed with concentrated sulphuric acid; *phenyldithiodiazoloneacetonylsulphide*,



melts at  $98-99^\circ$ , crystallises from dilute alcohol in yellowish needles, dissolves somewhat readily in the ordinary solvents, and is indifferent towards acids and bases. Methyl ethyl ketone reduces the hydro-sulphamine, with liberation of ammonia, and gives the *mercaptol*,  $CMeEt(S \cdot C_8H_5N_2S_2)_2$ , as a yellowish, aromatic oil; methyl propyl ketone gives a similar product. Acetophenone behaves like acetone and gives the *substance*,  $C_8H_5N_2S_2 \cdot S \cdot NH \cdot CMePh \cdot S \cdot C_8H_5N_2S_2$ , which crystallises from alcohol in stout prisms and melts at  $158-159^\circ$ .

T. M. L.

**Diazole Group. VI. Paratolyldiazolonethiol.** By MAX BUSCH and H. VON BAUR-BREITENFELD (*J. pr. Chem.*, 1899, [ii], 60, 206-212).

—*Paratolyldithiodiazolonethiol*,  $C_7H_7 \cdot N < \begin{smallmatrix} N=C \cdot SH \\ CS \cdot S \end{smallmatrix}$ , crystallises from a

mixture of ether and light petroleum in yellowish needles, melts at  $155^\circ$ , and rapidly oxidises to the bisulphide when exposed to the air. The *benzoyl* derivative forms white needles, and melts at  $100^\circ$ ; the *acetyl* derivative forms long, yellowish, glistening needles, and melts at  $158^\circ$ . The *methyl ether* crystallises from alcohol in white needles and melts at  $115-116^\circ$ . The *bisulphide* crystallises from a mixture of

alcohol and chloroform in minute, yellow needles, and from alcohol and benzene in clear, orange-yellow prisms, melts at 139—140°, and becomes red on prolonged exposure to the air. The thiol is reduced by sodium

amalgam to paratolythiodiazolinethiol,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot SH \\ \diagdown \\ CH_2 \cdot S \end{smallmatrix}$ , and is oxidised by potassium permanganate to *paratolyldithiodiazolonesulphonic acid*,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot SO_3H \\ \diagdown \\ CS \cdot S \end{smallmatrix}$ , which crystallises from a mixture of alcohol and light petroleum, cooled in a freezing mixture, in slender, glistening needles; the *potassium* and *barium* salts are described.

*Paratolyldithiodiazolonehydrosulphamine*,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot S \cdot NH_2 \\ \diagdown \\ CS \cdot S \end{smallmatrix}$ , prepared by the action of alcoholic ammonia on the bisulphide, melts at 150°, dissolves fairly readily in chloroform or ether, and crystallises from alcohol or benzene in slender, colourless needles; it becomes yellowish on prolonged exposure to the air, and is decomposed by acids in alcoholic solution into the bisulphide and an ammonium salt. *Paratolyldithiodiazolonethylhydrosulphamine*,  $C_9H_7N_2S_2 \cdot S \cdot NH_2Et$ , forms slender, white needles, and melts at 118—119°; the *dimethylhydrosulphamine*,  $C_9H_7N_2S_2 \cdot S \cdot NMe_2$ , forms slender, white needles, and melts at 85°, and readily decomposes into the bisulphide and the amine; diamylamine has a reducing action, and gives only the diamylamine salt of the original thiol.

*Paratolyldithiodiazolonethiol paramidophenylic ether*,  $C_9H_7N_2S_2 \cdot S \cdot C_6H_4 \cdot NH_2$  [ $NH_2 : S = 1 : 4$ ], separates from dilute acetic acid in stout, glistening, slightly yellowish crystals, dissolves readily in benzene or chloroform, less readily in alcohol or ether, and melts at 173°; the *hydrochloride* forms white, glistening needles; the *platinochloride* is an orange-yellow, micro-crystalline powder, and the diazo-compound forms a red *azo-dye* with  $\beta$ -naphthol.

*Paratolyldithiodiazolonethiol methylamidophenylic ether*,  $C_9H_7N_2S_2 \cdot S \cdot C_6H_4 \cdot NMe$ , melts at 184°, crystallises from alcohol in white needles, dissolves in benzene, chloroform, or acetic acid, and slightly in ether or ethylic acetate; the *nitrosamine* forms minute needles, melts at about 127°, and gives Liebermann's reaction. T. M. L.

**Diazole Group. VII. Orthotolyl- and  $\alpha$ - and  $\beta$ -Naphthyl-dithiodiazolonethiols.** By MAX BUSCH and HEINRICH MÜNKER (*J. pr. Chem.*, 1899, [ii], 60, 212—216).—*Orthotolyldithiodiazolonethiol*,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot SH \\ \diagdown \\ CS \cdot S \end{smallmatrix}$ , forms a white, crystalline precipitate, and dissolves readily in alcohol, ether, benzene, or chloroform. The *methylic ether* forms white needles and melts at 98°. The *bisulphide* crystallises from chloroform in beautiful, yellow needles or flakes. *Orthotolyldithiodiazolonethiol paramidophenylic ether*,  $C_9H_7N_2S_2 \cdot S \cdot C_6H_4 \cdot NH_2$ , forms white needles and melts at 128°.

*$\alpha$ -Naphthyl-dithiodiazolonethiol*,  $C_{10}H_7 \cdot N \begin{smallmatrix} N=C \cdot SH \\ \diagdown \\ CS \cdot S \end{smallmatrix}$ , melts at 127°.

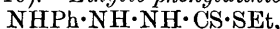
The *benzoyl* derivative crystallises from alcohol in minute, yellowish needles and melts at  $146^{\circ}$ . The *bisulphide* crystallises from a mixture of chloroform and alcohol in beautiful, yellow flakes and melts at  $228^{\circ}$ .

$\beta$ -*Naphthyl*dithiodiazolonethiol crystallises from benzene in colourless needles and melts at  $160^{\circ}$ . The *methylic* ether crystallises from alcohol in white needles and melts at  $112^{\circ}$ . The *bisulphide* forms yellow needles and melts at  $188^{\circ}$ . *Naphthyl*dithiodiazolonesulphonic acid,  $C_{10}H_7 \cdot N \begin{smallmatrix} \text{N}=\text{C} \cdot \text{SO}_3\text{H} \\ \text{CS} \cdot \text{S} \end{smallmatrix}$ , forms brownish flakes, and gives crystalline *potassium*, *barium*, and *lead* salts.

*Orthoanisyl*dithiodiazolonethiol,  $\text{OMe} \cdot C_6H_4 \cdot N \begin{smallmatrix} \text{N}=\text{C} \cdot \text{SH} \\ \text{CS} \cdot \text{S} \end{smallmatrix}$ , crystallises from a mixture of benzene and light petroleum in well-formed, transparent, yellowish prisms, and melts at  $119$ – $120^{\circ}$ . The *bisulphide* forms yellow needles and melts at  $174$ – $175^{\circ}$ . T. M. L.

**Diazole Group. VIII. Action of Ammonia and Aniline on Phenylmethylthiodiazoline Bisulphide.** By MAX BUSCH (*J. pr. Chem.*, 1899, [ii], 60, 216–217. Compare Abstr., 1896, i, 190).—Phenylmethylthiodiazoline bisulphide, when treated with alcoholic ammonia, gives sulphur, phenylthiosemicarbazide, and the ammonium derivative of phenylmethyldiazolinethiol. Aniline similarly gives sulphur, diphenylthiosemicarbazide, and the aniline derivative of the thiol. T. M. L.

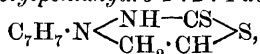
**Diazole Group. IX. Phenylthiocarbazine Acid and Benzoic Chloride.** By MAX BUSCH and J. BECKER (*J. pr. Chem.*, 1899, [ii], 60, 217–219).—*Ethylic phenylthiocarbazine*,



crystallises from alcohol in beautiful, transparent prisms and melts at  $127^{\circ}$ . The *benzylic* salt crystallises from benzene in splendid, transparent prisms and melts at  $164^{\circ}$ . The *benzoyl* derivative cannot be isolated, as it immediately loses water and gives diphenylisodithiodiazolone,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{CS} \\ \text{CPh} \cdot \text{S} \end{smallmatrix}$  (Abstr., 1896, i, 190); a second product

of the action of benzoic chloride on phenylthiocarbazine acid is *dibenzophenylhydrazide*,  $\text{NPhBz} \cdot \text{NHBz}$ , which crystallises from alcohol in glistening, white needles and melts at  $177$ – $178^{\circ}$ . T. M. L.

**Diazole Group. X. Diazolines from Paratolyldithiocarbazine Acid and its Ethereal Salts.** By MAX BUSCH [and E. LINGENBRINK] (*J. pr. Chem.*, 1899, [ii], 60, 219–225).—*Methylic paratolyldithiocarbazine*,  $C_7H_7 \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{SMe}$ , forms glistening, colourless needles and melts at  $149^{\circ}$ . The *ethylic* salt crystallises from alcohol in well-formed, transparent prisms and melts at  $128^{\circ}$ . The *benzylic* salt forms colourless needles, dissolves slightly in alcohol, and readily in ether or benzene, and melts at  $146^{\circ}$ . The action of ethylenic dibromide on the potassium salt does not give the ethylenic salt, but a ring compound, *paratolylpentahydro-1:2:4-diazathine*,



which melts at  $124^{\circ}$ , separates from a mixture of benzene and light

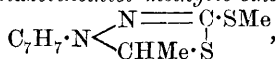
petroleum in bunches of pointed crystals, and dissolves fairly readily in the ordinary solvents, with the exception of light petroleum; alcoholic ferric chloride gives a dark blue coloration, and a black, amorphous mass is precipitated on adding water to the solution; the colour disappears on adding alkali.

Formaldehyde condenses with the potassium salt to form *paratolythiodiazolinethiol*,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot SH \\ | \\ CH_2 \cdot S \end{smallmatrix}$ , which crystallises from benzene in beautiful, white flakes, melts at  $80^\circ$ , but at  $103\text{--}105^\circ$  when kept overnight in a desiccator, dissolves readily in alcohol, benzene, ether, or chloroform, and slightly in light petroleum, and dissolves in cold caustic alkalis, but is decomposed, on warming, into the aldehyde and carbazinic acid. The *bisulphide* crystallises in orange-red needles on adding alcohol to a solution in chloroform, and melts at  $102^\circ$  to a red oil which at once becomes yellow owing to the decomposition of the bisulphide into the thiol, and the isodithiodiazolone. *Paratolylisodithiodiazolone*,  $C_7H_7 \cdot N \begin{smallmatrix} N=CS \\ | \\ CH \cdot S \end{smallmatrix}$ , is formed by decomposition of the bisulphide in chloroform solution at the ordinary temperature and rapidly on warming; it crystallises in bunches of yellow needles, melts at  $198^\circ$ , and dissolves only sparingly in the ordinary solvents; the *methiodide* crystallises from chloroform in long, yellow needles, and when treated with alkalis, gives a yellowish-brown, oily base.

*Paratolylmethylthiodiazolinethiol*,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot SH \\ | \\ CHMe \cdot S \end{smallmatrix}$ , prepared by the condensation of acetaldehyde with paratolylcarbazine acid, crystallises from benzene in beautiful, colourless, transparent prisms, and melts at  $143^\circ$ . The *bisulphide* crystallises from a mixture of alcohol and chloroform in splendid, glistening, orange-yellow flakes, and melts at  $123^\circ$ ; it is fairly stable, but decomposes on heating at  $100^\circ$ .

*Paratolylmethylisodithiodiazolone*,  $C_7H_7 \cdot N \begin{smallmatrix} N=CS \\ | \\ CMe \cdot S \end{smallmatrix}$ , crystallises from a mixture of chloroform and alcohol in silvery, grey flakes and melts at  $216^\circ$ . When heated with aniline, the bisulphide gives sulphur and paratolylphenylsemicarbazide.

*Paratolylmethylthiodiazolinethiol methylic ether*,



prepared by condensation of acetaldehyde with methylic paratolyldithiocarbazinate, crystallises in colourless, glistening needles or small flakes, melts at  $50^\circ$ , and dissolves readily in the ordinary solvents. Benzaldehyde condenses similarly to *tolylphenylthiodiazolinethiol methylic ether*,  $C_7H_7 \cdot N \begin{smallmatrix} N=C \cdot SMe \\ | \\ CHPh \cdot S \end{smallmatrix}$ , which crystallises in stout, glistening, white needles and melts at  $99^\circ$ . The corresponding *ethylc* salt crystallises similarly and melts at  $89^\circ$ ; the *benzylc* salt melts at  $105^\circ$ , is much less soluble in alcohol, and crystallises in hair-like needles.

T. M. L.

**Diazo Group. XI. Orthanisyl- and  $\alpha$ - and  $\beta$ -Naphthyl-dithiocarbazinic Acids and their Derivatives.** By MAX BUSCH and FRIEDRICH BEST (*J. pr. Chem.*, 1899, [ii], 60, 225—232).—*Potassium orthanisyl-dithiocarbazinate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{SK}$ , crystallises in white, microscopic flakes. With ethylenic bromide, it forms *orthanisyl-pentahydro-1 : 3 : 5-dithiodiazine*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\left\langle\begin{array}{c} \text{NH} - \text{CS} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}\right\rangle\text{S}$ ; this crystallises from dilute alcohol in long, pointed forms, which, like the solution, become green on exposure to the air, and from light petroleum in stout, white needles, dissolves very readily in all other solvents, and melts at  $85-86^\circ$ ; the *acetyl* derivative separates from benzene in stout, white crystals, and melts at  $150^\circ$ ; the *hydrochloride* forms white needles and melts at  $163-164^\circ$ .

*Orthanisylmethylthiodiazolinethiol*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\left\langle\begin{array}{c} \text{N} = \text{C} \cdot \text{SH} \\ \text{CHMe} \cdot \text{S} \end{array}\right\rangle$ , crystallises from benzene in beautiful, large, yellowish prisms, melts at  $149^\circ$ , and dissolves readily in alcohol.

*Potassium  $\alpha$ -naphthyl-dithiocarbazinate*,  $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{SK}$ , melts at  $118^\circ$ , dissolves readily in alcohol or water, and crystallises in white flakes, but soon becomes yellow on exposure to the air. The *methyl* salt melts with decomposition at  $160^\circ$ , crystallises in white needles, has a characteristic odour suggestive of fresh mushrooms, and gradually becomes blue-grey on exposure to air. The *ethyl* salt is similar, and melts at  $124^\circ$ . The *benzyl* salt melts at  $127^\circ$  and crystallises from alcohol in white needles.  *$\alpha$ -Naphthyl-pentahydro-1 : 3 : 5-dithiodiazine*,  $\text{C}_{10}\text{H}_7\cdot\text{N}\left\langle\begin{array}{c} \text{NH} - \text{CS} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}\right\rangle\text{S}$ , separates from benzene in stout, yellowish crystals, melts at  $148^\circ$ , dissolves in hot alcohol, and soon becomes green unless quite pure; the *hydrochloride* forms glistening, yellowish needles, melts at  $182-183^\circ$ , and is decomposed by water.

*$\alpha$ -Naphthylphenyl-dithioisodiazoline*,  $\text{C}_{10}\text{H}_7\cdot\text{N}\left\langle\begin{array}{c} \text{N} - \text{CS} \\ \text{CPh} \cdot \text{S} \end{array}\right\rangle$ , prepared by the action of benzoic chloride on the carbazinic acid, crystallises from a mixture of chloroform and alcohol in bunches of golden-yellow needles, melts at  $207^\circ$ , is only dissolved largely by hot chloroform, and is hydrolysed by caustic alkalis to benzoic acid and  *$\alpha$ -naphthyl-dithiocarbazinic acid*.

No condensation could be effected with formaldehyde, but acetaldehyde gave  *$\alpha$ -naphthylmethylthiodiazolinethiol*,  $\text{C}_{10}\text{H}_7\cdot\text{N}\left\langle\begin{array}{c} \text{N} = \text{C} \cdot \text{SH} \\ \text{CHMe} \cdot \text{S} \end{array}\right\rangle$ , this crystallises from a mixture of ether and light petroleum in transparent, yellowish, efflorescent needles, dissolves readily in alcohol, benzene, or chloroform, and slightly in light petroleum, and melts at  $164^\circ$ . The *bisulphide* was precipitated, on adding ferric chloride to the alcoholic solution, in yellow flocks, but was obtained as a yellow oil on attempting to recrystallise it. The *methyl ether* melts at  $108^\circ$ , crystallises from light petroleum in glistening, transparent, well-formed needles or prisms, and dissolves readily in alcohol, ether, or benzene.

Benzaldehyde does not condense with methylic  $\alpha$ -naphthylthiocarbazine at  $100^\circ$ , and at  $120^\circ$  a non-crystalline product is obtained.

*Potassium  $\beta$ -naphthylthiocarbazine*,  $C_{10}H_7 \cdot NH \cdot NH \cdot CS \cdot SK$ , dissolves readily in water, crystallises from alcohol in glistening needles, and melts at  $112^\circ$ . The *methylic* salt melts at  $143$ — $144^\circ$ , crystallises in small, white needles, and resembles the  $\alpha$ -compound. The *ethyl* salt melts at  $142$ — $143^\circ$ . The *benzyl* salt melts at  $171^\circ$ . The  *$\beta$ -naphthylpentahydrodithiodiazine*,  $C_{10}H_7 \cdot N < \begin{smallmatrix} NH-CS \\ CH_2 \cdot CH_2 \end{smallmatrix} > S$ , is very sensitive to oxygen and the solutions immediately become bluish-green; the *hydrochloride* separates from alcohol in yellow needles and melts at  $200$ — $201^\circ$ .

*$\beta$ -Naphthylphenylisodithiodiazolone*,  $C_{10}H_7 \cdot N < \begin{smallmatrix} N-CS \\ CPh \cdot S \end{smallmatrix} >$ , separates from a mixture of chloroform and alcohol in yellow, radiating needles, melts at  $212$ — $213^\circ$ , and closely resembles the  $\alpha$ -compound.

*$\beta$ -Naphthylthiodiazolinethiol*,  $C_{10}H_7 \cdot N < \begin{smallmatrix} N=C \cdot SH \\ CH_2 \cdot S \end{smallmatrix} >$ , crystallises from benzene in yellowish prisms and melts at  $115^\circ$ .

*$\beta$ -Naphthylmethylthiodiazolinethiol*,  $C_{10}H_7 \cdot N < \begin{smallmatrix} N=C \cdot SH \\ CHMe \cdot S \end{smallmatrix} >$ , melts at  $164$ — $165^\circ$ , and crystallises from benzene in clear, yellowish prisms; it dissolves in cold caustic soda, but on warming is decomposed with separation of acetaldehyde. T. M. L.

**Diazole Group. XII. Phenylthiodiazolinethiol.** By MAX BUSCH and ALFRED STERN (*J. pr. Chem.*, 1899, [ii], 60, 233—235).—*Phenylthiodiazolinethiol*,  $NPh < \begin{smallmatrix} N=C \cdot SH \\ CMe_2 \cdot S \end{smallmatrix} >$ , formed by condensation of acetone with phenylthiocarbazine, melts at  $135$ — $136^\circ$ , separates from a mixture of benzene and light petroleum in large, well-formed crystals, and dissolves readily in ordinary solvents. The action of iodine on the potassium salt breaks the ring and gives the bisulphide of phenylthiocarbazine (Abstr., 1896, i, 677), and not the bisulphide of the thiol; similarly, methylic iodide does not give the methylic salt of the thiol, but methylic phenylthiocarbazine; the dialkylated diazoline ring is therefore somewhat unstable.

*Phenylmethylthiodiazolinethiol*,  $NPh < \begin{smallmatrix} N=C \cdot SH \\ CMeEt \cdot S \end{smallmatrix} >$ , crystallises from a mixture of benzene and light petroleum in white needles, melts with frothing at  $158^\circ$ , and in solubility resembles the dimethyl derivative.

No condensation occurs in the case of acetophenone or when the etheric salts are used in place of the carbazine acid. T. M. L.

**Diazole Group. XIII. Formation of Diazoles from Phenylthiocarbazine and Phenylthiocarbazine Acids.** By MAX BUSCH and ALFRED STERN (*J. pr. Chem.*, 1899, [ii], 60, 235—243. Compare Fischer, Abstr., 1878, 307).—*Potassium phenylthiocarbazine* crystallises from alcohol in beautiful, glistening needles and melts with decomposition at  $243^\circ$ ; it is immediately decomposed by mineral acids with

liberation of carbonic anhydride, but is fairly stable in the dry state; the etheric salts could not be prepared by the action of alkyl iodides on the potassium salt, as a similar decomposition of the acid took place. The action of phosgene on the potassium salt led to the formation of diphenylurazine, and not of the phenylhydroxydiazolone,

$\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OH} \\ \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ , which was expected. The action of acetaldehyde

caused the decomposition of the acid and led to the formation of phenylethylidenehydrazine. Carbon bisulphide gave phenyldithiodiazolonethiol by interaction with the phenylhydrazine liberated by the decomposition of the carbazinic acid. Diazolones can, however, be prepared from the stable ethylic salt of phenylcarbazine acid (Heller, Abstr., 1891, 1212).

*Ethylic chlorocarbonylphenylcarbazine*,  $\text{COCl}\cdot\text{NPh}\cdot\text{NH}\cdot\text{COOEt}$ , prepared by the action of carbonyl chloride on ethylic phenylcarbazine, melts at  $101^\circ$ , crystallises from light petroleum in glistening, white needles, and dissolves readily in the ordinary solvents. By distillation, or by the action of alkalis, it loses hydrogen chloride, and gives

*ethoxyphenyldiazolone*,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OEt} \\ \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ ; this crystallises from alcohol

in beautiful, large, clear prisms, dissolves readily in alcohol, ether, benzene, or chloroform, slightly in light petroleum, and melts at  $72^\circ$ .

*Ethylic chlorothiocabonylphenylcarbazine*,  $\text{CSCl}\cdot\text{NPh}\cdot\text{NH}\cdot\text{COOEt}$ , separates from a mixture of benzene and light petroleum in stout, colourless crystals, dissolves readily in most solvents, and melts at  $116^\circ$ , giving off bubbles of gas. By the action of alkali, it yields *ethoxy-*

*phenylpseudothiodiazolone*,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{OEt} \\ \diagdown \\ \text{CS}\cdot\text{O} \end{smallmatrix}$ ; this is less stable than

the corresponding oxygen compound, and decomposes when heated to the boiling point; it crystallises from alcohol in large, white needles and melts at  $29^\circ$ . Ethylic phenylcarbazine does not condense with acetaldehyde at the ordinary temperature, and on heating decomposition occurs.

*Potassium phenylthiocarbazine*,  $\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{SK}$  (compare Heller, *loc. cit.*), separates from alcohol in stout, white crystals containing 1 mol. of alcohol. The *bisulphide* is an insoluble, white compound. Phenylethylidenehydrazine is produced when acetaldehyde acts on potassium phenylthiocarbazine, owing to the decomposition of the acid; the etheric salts can, however, be prepared by the action of alkyl iodides on the potassium salt. The *methylic* salt crystallises from alcohol in beautiful, white needles, dissolves readily in the ordinary solvents, except light petroleum, and melts at  $152^\circ$ . The *ethylic* salt forms white needles and melts at  $113^\circ$ . The *benzylic* salt is less soluble in alcohol, and crystallises in slender, white needles; it melts at  $170^\circ$ . By the action of carbonyl chloride on the methylic salt,

*phenyldiazolonethiol methylic ether*,  $\text{C}_6\text{H}_5\cdot\text{N} \begin{smallmatrix} \text{N}=\text{C}\cdot\text{SMe} \\ \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ , is produced;

it melts at  $55\text{--}56^\circ$ , dissolves readily in alcohol, benzene, ether, or chloroform, and slightly in light petroleum, but not in water.

T. M. L.

**Triazan Derivatives.** By HUGO VOSWINCKEL (*Ber.*, 1899, 32, 2481—2492; 2770).—*Phenylethylideneoxycyclotriazan*,  $\text{NPh} \begin{smallmatrix} \text{NO} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CHMe}$ ,  $\text{NPh} \begin{smallmatrix} \text{N(OH)} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{CHMe}$ , or  $\text{NPh} \begin{smallmatrix} \text{NH} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$ , is produced by adding an aqueous solution of aldehyde-ammonia to an alcoholic solution of phenylnitrosohydrazine and heating the mixture for a few minutes on the water-bath; ammonia is evolved, and the residue, after distilling off the alcohol, is crystallised from dilute alcohol. It forms flexible, orange needles, and melts at  $116^\circ$ , the melting point being perceptibly influenced by the rate of heating. It is soluble in ether, benzene, or hot water, and is reprecipitated by acids from its solution in dilute alkalis; it is volatile in steam and distils without decomposition. The *sodium* derivative is formed by adding an excess of sodium hydroxide to a solution of the condensation product in absolute alcohol or in dilute caustic soda; it separates in light yellow needles, which are soluble in water, alcohol, or hot acetone, but not in ether or benzene; it detonates on heating.

The *methyl* derivative,  $\text{NPh} \begin{smallmatrix} \text{NMe} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}$ , obtained by heating an aqueous solution of the preceding compound with methylic iodide, crystallises in dark orange needles and melts at  $90^\circ$ ; it is soluble in the ordinary organic solvents.

*Phenyldimethylcyclomethylenetriazan hydrochloride*,  $\text{NPh} \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CHMe, HCl}$ , produced by reducing the preceding compound with stannous chloride, crystallises from alcohol in pale yellow, highly refractive needles melting at  $281^\circ$ ; it is very soluble in water and does not yield condensation products with benzaldehyde. The base is a colourless oil becoming brown on exposure to air. When the reduction is carried further, another base is formed, which, in all probability, has the constitution  $\text{NH}_2 \cdot \text{NPh} \cdot \text{NMe} \cdot \text{CH}_2\text{Me}$ ; it condenses readily with benzaldehyde.

*Phenylmethyloxycyclomethylenetriazan*,  $\text{NPh} \begin{smallmatrix} \text{N(OH)} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CHMe}$ , obtained by reducing the original condensation product with aqueous ammonium sulphide or stannous chloride, dissolves in alcohol or benzene, but not in water or dry ether, crystallises in leaflets, and melts at  $130^\circ$ ; by oxidising agents, such as nitrous acid, it is reconverted into the parent substance, and this change is also effected by repeated crystallisation from dilute alcohol. The compound is basic, and its *hydrochloride* forms colourless prisms and melts at  $174^\circ$ .

*Chlorophenylmethyloxycyclomethylenetriazan hydrochloride* separates in reddish-white needles from a solution of phenylethylideneoxycyclotriazan in concentrated hydrochloric acid; it melts at  $174^\circ$ . The *base*,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \begin{smallmatrix} \text{N(OH)} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CHMe}$ , is readily soluble in alcohol, ether, or benzene, but insoluble in water; it melts at  $131^\circ$ .

*Chlorophenylethylideneoxycyclotriazan*, whose constitution may be



represented by  $C_6H_4Cl \cdot N \begin{smallmatrix} \diagup NO \\ \diagdown N \end{smallmatrix} CHMe$ , or the other tautomeric formulæ corresponding with those of phenylethylideneoxycyclotriazan, is obtained by boiling the preceding compound with water or by crystallising from hot alcohol; it forms orange needles, melts at  $189^\circ$ , dissolves in alcohol, ether, benzene, or dilute alkalis, but not in water; reducing agents reconvert it into the parent substance.

The corresponding bromo-compounds,  $C_8H_{10}ON_3Br$  and  $C_8H_8ON_3Br$ , melt at  $128^\circ$  and  $195^\circ$  respectively.

*Phenylmethylecyclohexylmethylenetriazan hydrochloride* is prepared by reducing phenylmethyloxycyclohexylmethylenetriazan with stannous chloride; it crystallises in silky needles containing  $1H_2O$ , and melts at  $140^\circ$ ; when heated to  $105^\circ$ , it becomes anhydrous and then melts at  $205^\circ$ .

The base,  $NPh \begin{smallmatrix} \diagup NH \\ \diagdown NH \end{smallmatrix} CHMe$ , is an oil; its salts can be decomposed by soda or potash, but not by ammonia.

*Phenylethyltriazan hydrochloride*,  $NH_2 \cdot NPh \cdot NH \cdot CH_2Me, HCl$ , obtained on reducing phenylmethoxycyclohexylmethylenetriazan with stannous chloride, is separated from the admixed phenylhydrazine hydrochloride by fractional crystallisation; the hydrochloride of the triazan is the more soluble; it crystallises in colourless needles and melts at  $185^\circ$ . The base is an easily decomposable oil; its salts are not decomposed by ammonia, and with dilute acids intense reddish colorations are developed.

The *benzylidene* compound,

$CHPh \cdot N \cdot NPh \cdot NH \cdot CH_2Me$ , produced by mixing together benzaldehyde and the base at ordinary temperatures, crystallises in pale yellow needles which redden on exposure to air; it melts at  $163^\circ$ .

*Phenyltriazan hydrochloride*,  $NH_2 \cdot NPh \cdot NH_2, HCl$ , is separated by fractional crystallisation from the mixture of hydrochlorides obtained by the ultimate reduction of phenylethylideneoxycyclotriazan with ammonium sulphide; it crystallises in white needles and melts at  $220^\circ$ .

*Paratolylethylideneoxycyclotriazan*, prepared by condensing paratolynitrosohydrazine with aldehyde ammonia, crystallises in flexible, pale orange needles and melts at  $135^\circ$ ; it closely resembles its lower homologue.

*Paratolylmethyloxycyclohexylmethylenetriazan*, obtained by reducing the preceding compound with ammonium sulphide, crystallises in silvery, white needles and melts at  $122^\circ$ ; it is soluble in the ordinary organic solvents, but not in water.

G. T. M.

**Alkaloids contained in *Anagyris Fœtida*.** By MAX KLOSTER-MANN (*Chem. Centr.*, 1899, i, 1130; from *Diss. Marburg*, 1898. Compare *Abstr.*, 1896, i, 657).—By evaporating the alcoholic extract of the seeds of *Anagyris fœtida*, precipitating the aqueous solution with lead acetate, and decomposing the precipitate with hydrogen sulphide, a mixture of cytisine and anagyrine is obtained, from which the latter may be separated by dissolving in water acidified with hydrochloric acid and precipitating as the mercurichloride, whilst the former is isolated by making the solution alkaline and extracting with chloroform.

Cytisine,  $C_{11}H_{14}ON_2$ , crystallises from light petroleum in white needles and melts at  $152-153^\circ$ . The *nitrate*,  $C_{11}H_{14}ON_2 \cdot HNO_3 + H_2O$ , crystallises from a mixture of alcohol and ether in long, white needles, and has specific rotatory power  $[\alpha]_D - 81^\circ 29'$  when  $p = 3.5112$ . The *platinochloride*,  $(C_{11}H_{14}ON_2)_2 \cdot H_2PtCl_6$ , crystallises in yellow needles. The *aurichloride*,  $C_{11}H_{14}ON_2 \cdot HAuCl_4$ , crystallises from water in yellow needles and melts at  $220^\circ$ . *Anagyryne mercurichloride*,  $C_{15}H_{22}ON_2 \cdot HHgCl_2$ , separates from hot water in nodular crystals and melts at  $233-234^\circ$ . Anagyryne is prepared from the preceding compound by decomposing it with hydrogen sulphide and treating with alkali, but could not be obtained in a crystalline form. The *hydrochloride*,  $C_{15}H_{22}ON_2 \cdot HCl + H_2O$ , crystallises in rhombic plates, is easily soluble in water or alcohol, insoluble in ether or chloroform, and has a specific rotatory power  $[\alpha]_D - 142^\circ 28'$  when  $p = 1.8140$ . The *hydrobromide*,  $C_{15}H_{22}ON_2 \cdot HBr + H_2O$ , has properties similar to those of the hydrochloride and melts above  $235^\circ$ . The *nitrate*,  $C_{15}H_{22}ON_2 \cdot HNO_3 + H_2O$ , crystallises from a mixture of alcohol and ether in long, white needles, and has specific rotatory power  $[\alpha]_D - 126^\circ 2'$  when  $p = 1.00$ . The *platinochloride*,  $C_{15}H_{22}ON_2 \cdot H_2PtCl_6 + 1\frac{1}{2}H_2O$ , forms ruby-red needles, does not melt below  $235^\circ$ , and is slightly soluble in water. The *aurichloride*,  $C_{15}H_{22}ON_2 \cdot HAuCl_4$ , forms a bulky, crystalline precipitate and melts at  $210-211^\circ$ . *Anagyryne methiodide*,  $C_{15}H_{22}ON_2 \cdot MeI$ , crystallises from methylic alcohol in snow-white needles and melts above  $235^\circ$ . The *platinochloride*,  $C_{15}H_{22}ON_2 \cdot MeI \cdot H_2PtCl_6 + H_2O$ , crystallises from dilute hydrochloric acid in yellowish-red needles and melts above  $235^\circ$ . The results of experiments on the introduction of methyl groups, together with other evidence, indicate that anagyryne is a bitertiary base. *Dibromanagyryne hydrobromide*,  $C_{15}H_{20}ON_2Br_2 \cdot HBr$ , prepared by treating an alcoholic solution of anagyryne hydrobromide with bromine and heating the resulting precipitate with alcohol, crystallises in silky, white needles, melts above  $235^\circ$ , and is easily soluble in alcohol or water. *Dibromanagyryne platinochloride*,  $C_{15}H_{20}ON_2Br_2 \cdot H_2PtCl_6$ , forms reddish-yellow needles and melts above  $235^\circ$ . The *aurichloride* separates in reddish-yellow needles and melts at  $223^\circ$ . When the properties of anagyryne are compared with those of cytisine, it is evident that the former is probably butyleytisine.

E. W. W.

**Isomerism in the Cinchonine Group.** By ZDENKO H. SKRAUP (*Monatsh.*, 1889, 20, 571—584).—A critical examination of the alleged isomerides of cinchinone. Hesse's  $\alpha$ - and  $\beta$ -isocinchonine (*Abstr.*, 1893, i, 677) are easily separated in the form of the dihydriodides, that of  $\alpha$ -isocinchonine being easily soluble and that of  $\beta$ -isocinchonine almost insoluble in cold water. These two, and the two isomerides  $\delta$ - and  $\epsilon$ -cinchonine obtained by Cordier (*Monatsh.*, 1898, 19, 472) from *hydrobromocinchonine*, are well characterised by their specific rotatory powers, and there can be no doubt that they are actual isomerides of cinchonine.

Cordier's tautocinchonine (*loc. cit.*) is very similar to cinchonine, but the differences in the solubilities of the two bases in alcohol and of their sulphates in water point to tautocinchonine being a true isomeride of cinchonine. Hesse's "apocinchonine," "apoisocincho-

nine" and "isoapocinchonine" are one and the same compound, which is identical with Lippmann and Fleissner's allocinchonine (Abstr., 1893, i, 738). Allocinchonine is well characterised by the sparing solubility of its normal sulphate in water (1 part in 120 at 20°). The "cinchonifine" of Jungfleisch and Léger (Abstr., 1888, 380) is probably cinchotine, with which Hesse's pseudocinchonine is identical (von Arlt, this vol., i, 962).

After a close comparison of the sulphate and platinochloride of Hesse's homocinchonine with the corresponding compounds of cinchonine, the author comes to the opinion that the two bases are identical.

Jungfleisch and Léger (Abstr., 1892, 1253) have stated that Hesse's diapocinchonine is a mixture of  $\alpha$ - and  $\beta$ -isocinchonine. This is disputed by Hesse (*loc. cit.*), but now confirmed by the author, who has separated  $\alpha$ - and  $\beta$ -isocinchonine from "diapocinchonine" by means of the dihydriodides.

The directions given by Pum (Abstr., 1893, i, 181) for the preparation of  $\beta$ - and  $\gamma$ -cinchonine were followed, but the substance obtained was allocinchonine.

Hydrochlorapocinchonine and hydrochlorapoisocinchonine were prepared according to Hesse's method. From a redetermination of the solubilities of the bases and their salts, there is no doubt that they are both identical with hydrochlorocinchonine. This, however, differs so much from hydrochloro- $\alpha$ -isocinchonine that there is no possibility that they are identical.

R. H. P.

**Molecular Transformations: the Transformation of Cinchonine into  $\alpha$ -Isocinchonine.** By ZDENKO H. SKRAUP (*Monatsh.*, 1899, 20, 585—616).—If hydrochloric, hydrobromic, or hydriodic acid acts on cinchonine at the ordinary temperature, a portion of the cinchonine is transformed into  $\alpha$ -isocinchonine and another portion converted into an additive compound. In this paper, the data of a large number of experiments with acids of ten and fourteen times normal strength and the quantities of  $\alpha$ -isocinchonine and the addition products thus formed at different intervals are given. Much time is taken for the completion of the reactions, but only the results obtained at the beginning of the actions are of any value, since a secondary reaction between the  $\alpha$ -isocinchonine and the acid interferes after a short time. The velocities with which hydriodic, hydrobromic, and hydrochloric acids form the additive compounds are in the proportion of 200,000 : 400 : 1. The quantities of cinchonine transformed into  $\alpha$ -isocinchonine in the same time by these acids are in the proportion of 10 : 2.6 : 1, and the ratio of the amount of cinchonine transformed into  $\alpha$ -isocinchonine to that converted into an additive compound varies for each acid, but is independent of the concentration, time, or temperature.

This transformation cannot be referred to the action of ions, for the amounts of cinchonine transformed into  $\alpha$ -isocinchonine by the three acids bear no proportion to their electrical conductivities. Further, it is noteworthy that nitric acid will not effect the transformation. The results show that this molecular transformation is dependent on

a second reaction taking place at the same time (compare the author's views on the conversion of maleic acid into fumaric acid (Abstr., 1891, 1338).

*Cinchonine dinitrate*,  $C_{19}H_{22}N_2O_2 \cdot (HNO_3)_2$ , is formed when a solution of cinchonine hydrogen sulphate is treated with barium nitrate, filtered, and evaporated. On the addition of alcohol, the salt crystallises out in the form of large, lustrous prisms. R. H. P.

**Pseudocinchonine and the Behaviour of Hydrochlorocinchonine.** By F. VON ARLT (*Monatsh.*, 1899, 20, 425—449).—This is a repetition of Hesse's work on the same subject (Abstr., 1893, i, 677). The author treats cinchonine dihydrochloride with hydrochloric acid of sp. gr. 1.160 at 100° (instead of at 80°). About 29 per cent. of the cinchonine is converted into hydrochlorocinchonine dihydrochloride, which crystallises out of the solution. The mother liquor is treated according to Hesse's method with ammonia and ether. 64 per cent. of the cinchonine is thus obtained as pseudocinchonine and about 8 per cent. as a mixture of bases easily soluble in ether. The crude pseudocinchonine is purified by treatment of its crude hydrochloride with alcoholic potash, reconversion of the base into the hydrochloride, and crystallisation of the latter. By neutralising and crystallising the mother liquor, Hesse's apoisocinchonine can be obtained. From its melting point (214—217°) and the solubility (1 pt. in 117.07 pts. of water) of its sulphate ( $C_{19}H_{22}ON_2$ )<sub>2</sub> · H<sub>2</sub>SO<sub>4</sub> + 1½ H<sub>2</sub>O, there is little doubt of its identity with Lippmann and Fleissner's allocinchonine (Abstr., 1893, i, 738).

The mother liquor obtained after treating the crude pseudocinchonine hydrochloride with alcoholic potash yields another alkaloid. This melts at 141°, has a specific rotatory power in alcoholic solution ( $p=1$ )  $[\alpha]_D +140.7^\circ$  at 20°, and is probably identical with Cordier's  $\delta$ -cinchonine (*Monatsh.*, 1898, 19, 473).

Pure pseudocinchonine is proved to be identical with cinchotine. It melts at 265—267.5° and thus agrees with the melting point of cinchotine found by Forst and Böhringer (Abstr., 1881, 620, and 830) and by Pum (*Monatsh.*, 1895, 16, 70).

The solubility of the base in alcohol is 1 pt. in 218.9 pts., while that of cinchotine is 1 pt. in 221.5 pts. The hydrochloride (melting at 216°), the hydriodide (melting at 127°), and the dihydriodide (melting at 258°) are identical with the corresponding compounds of cinchotine. *Cinchotine methiodide*,  $C_{19}H_{24}ON_2 \cdot MeI$ , forms hard, white prisms melting at 244—246°. The *hydriodide of cinchotine methiodide*,  $C_{19}H_{24}ON_2 \cdot MeI \cdot HI$ , crystallises in compact, yellow prisms which turn brown at 221° and decompose at 227—229°. It does not yield the methiodide on treatment with ammonia or sodium carbonate.

Cinchotine, when oxidised by potassium permanganate in acid solution, yields formic acid and a dark brown syrup, which, however, contains no cinchotenine.

The author's treatment of cinchonine dihydrochloride yields a much smaller proportion of the bases easily soluble in ether than Hesse obtained. The formation of  $\alpha$ -isocinchonine in this manner is confirmed by the author, who also finds small quantities of  $\beta$ -isocin-

chonine (probably formed by the action of the hydrochloric acid at the higher temperature on  $\alpha$ -isocinchonine).

Hesse's work on the action of alcoholic potash on hydrochlorocinchonine has also been repeated.  $\alpha$ -Isocinchonine is separated from the mixture of three bases thus obtained by its solubility in ether. The two bases insoluble in ether are fractionated by crystallisation from alcohol. The one melts at  $246^{\circ}$ , has a specific rotatory power when dissolved in two volumes of alcohol and one of chloroform ( $p = 3$ )  $[\alpha]_{D^{20}} + 215.51^{\circ}$ , dissolves in 120.4 pts. of water, and is either cinchonine, or more probably Cordier's tautocinchonine (*loc. cit.*). Its sulphate,  $(C_{19}H_{22}ON_2)_2 \cdot H_2SO_4 + 2H_2O$ , dissolves in 61.18 pts. of water. The other base agrees in its properties with Hesse's apoisocinchonine and Lippmann and Fleissner's allocinchonine, with the exception that its sulphate has the composition  $(C_{19}H_{22}ON_2)_2 \cdot H_2SO_4 + 4H_2O$ .

Similar results were obtained by hydrolysing hydrochlorocinchonine with alcoholic silver nitrate. The proportion, however, of the bases insoluble in ether is in this case much larger. R. H. P.

**Cocaine.** By FRITZ GÜNTHER (*Chem. Centr.*, 1899, i, 848; from *Ber. pharm. Ges.*, 9, 38—43. Compare *Pharm. Centr.-Halle*, 39, 1).—Mac-Lagan's reaction for cocaine is useless for the valuation of the commercial article, and is most probably dependent on the presence of another base, for pure cocaine hydrochloride, when dissolved in 1000 parts of water, does not separate in a crystalline form on the addition of ammonia. A considerable quantity of a base which melts at  $110$ — $111^{\circ}$  and, according to Salkowski, acts physiologically like cocaine itself, has been isolated from cocaine. Mixtures of this base with cocaine dissolve like a homogeneous compound, and both bases crystallise from such solutions in apparently perfectly homogeneous, transparent prisms. From mixtures containing larger proportions of cocaine, the bases may be separated directly, although with difficulty, by means of light petroleum; a better separation is effected by dissolving in alcohol, neutralising with a solution of hydrogen chloride in alcohol, and then precipitating the hydrochloride with ether. The mother liquor then contains a mixture of bases from which the one of higher melting point may be isolated by means of light petroleum. At  $20^{\circ}$ , this base requires 2500—3000 parts of water for solution (cocaine 704), and its solubility in other solvents is also less than that of cocaine. It is almost as strongly lævotatory as cocaine, forms an aurichloride and picrate which cannot be distinguished from those of cocaine even under the microscope, and yields benzoic acid when decomposed by hydrochloric acid of sp. gr. 1.1. The results of analysis agree with the composition of a methylcocaine, and the compound is possibly an ethylbenzoylcegonine in which the hydrogen of the carboxyl group is replaced by ethyl. It is isomeric, but not identical, with cocethyline, which also gives Mac-Lagan's reaction. When treated with methylic alcohol, the benzoylcegonine prepared from this base yields methylbenzoylcegonine melting at  $101^{\circ}$ . The methylic alcohol, however, even after the most careful purification, was found to contain traces of ethylic alcohol

which easily condenses with benzoylecgonine, for even when obtained from the purest cocaine, benzoylecgonine was found also to yield bases of higher melting point when treated with this alcohol. It is probably for this reason, too, that the synthetically prepared commercial cocaine also gives MacLagan's reaction. A solution of 0.1 gram of cocaine hydrochloride in 85 c.c. of water should remain clear when 0.2 c.c. of ammonia solution is added.

E. W. W.

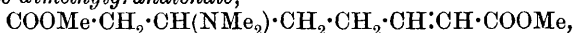
**Damascenine.** By HERBERT POMMEREHNE (*Arch. Pharm.*, 1899, 237, 475—480).—Damascenine is an alkaloid which occurs in the outer coat of the seeds of *Nigella Damascena*, L.; it has been isolated by Schneider (*Inaug. Diss. Erlangen*, 1890), who also prepared some of its salts. The author obtained it by digesting the uncrushed seeds for several days with 6 per cent. hydrochloric acid at 40—50°; the extract was then made alkaline with sodium carbonate and shaken gently with light petroleum, and the alkaloid removed from the petroleum solution (which has a blue fluorescence) by shaking with 8 per cent. hydrochloric acid; the acid extract was concentrated finally at 40°, and the hydrochloride of the alkaloid purified by recrystallisation; the seeds yielded 0.61 per cent. of the pure salt. The platinumchloride,  $(C_{10}H_{15}O_3N)_2 \cdot H_2PtCl_6$ , melts and decomposes at 194—198°; the aurichloride is very unstable, decomposing even in the dark. The alkaloid contains two methoxyl groups, and consequently has the formula  $C_8H_5ON(OMe)_2$ ; it resembles methylic anthranilate (Walbaum, this vol., i, 620) closely in many of its properties.

C. F. B.

**Hydrastine Pentiodide Hydriodide.** By HARRY MANN GORDIN and ALBERT B. PRESCOTT (*Arch. Pharm.*, 1899, 237, 439—446).—See this vol., ii, 826).

**Structure of the Alkaloids of the Pomegranate.** By ANTONIO PICCININI (*Gazzetta*, 1899, 29, ii, 104—114. Compare this vol., i, 829).

—*Dimethylic methylgranatate*, 
$$\begin{array}{c} CH_2-CH_2-CH_2 \\ | \quad | \quad | \\ COOMe \cdot CH \cdot NMe \cdot CH \cdot CH_2 \cdot COOMe \end{array}$$
 forms an almost colourless oil of a pungent, ethereal odour; it is soluble in dilute acids, gives no precipitate with platinic chloride, but with auric chloride forms a yellowish, oily precipitate. It combines slowly with methylic iodide, yielding *dimethylic methylgranatate methiodide*,  $C_{11}H_{19}O_4N \cdot MeI$ , which separates from alcohol in colourless prisms melting at 167°; it is soluble in cold water, and its solution in dilute sulphuric acid decolorises permanganate with extreme slowness. On heating this methiodide with alkali hydroxide or carbonate, *dimethylic dimethylgranatenate*,



is obtained as an oil which dissolves in dilute acids, gives an oily *aurichloride* and *picrate*, and combines readily with methylic iodide, forming a *methiodide*,  $C_{12}H_{21}O_4N \cdot MeI$ , which separates from alcohol in very thin leaflets melting at 143—144°. Dimethylic dimethylgranatenate in dilute sulphuric acid solution instantly decolorises permanganate solution. On boiling the methiodide with concentrated caustic alkali, trimethylamine and *homopiperilenedicarboxylic acid*,  $C_2H_4(CH \cdot CH \cdot COOH)_2$ , are obtained. The latter separates from

water in slender, microscopic, colourless needles melting at  $228^{\circ}$  with previous softening; when dissolved in dilute sodium carbonate solution, it is instantly oxidised by permanganate solution. Its *silver* salt,  $C_8H_8O_4Ag_2$ , forms a white powder which is insoluble in water and suffers change on exposure to light. On reducing homopiperilenedicarboxylic acid in caustic alkali solution by means of sodium amalgam, normal suberic acid is obtained. T. H. P.

**Methylgranatylamines.** By ANTONIO PICCININI and A. QUARTAROLI (*Gazzetta*, 1899, 29, ii, 115—123).—*Methylgranatylamine*,  $C_9H_{18}N_2$ , obtained by reducing methylgranatonine oxime by means of sodium amalgam and acetic acid, is a dense, colourless liquid which has a faint, basic odour, and at the ordinary pressure boils at  $235$ — $240^{\circ}$  with slight decomposition, but boils unchanged at  $160$ — $170^{\circ}$  under 60 mm. pressure. It is very soluble in water, and rapidly absorbs carbonic anhydride from the air with formation of a crystalline mass of carbamate. The *hydrochloride* forms a colourless, deliquescent mass, and the *aurichloride*,  $C_9H_{18}N_2 \cdot 2HAuCl_4$ , separates in tufts of yellow needles melting with slight decomposition at  $226^{\circ}$ , and soluble in boiling dilute hydrochloric acid; the *platinochloride* is deposited in golden-yellow spangles, which melt and decompose at  $260$ — $261^{\circ}$ , and are very soluble in dilute hydrochloric acid even in the cold. The *picrate* crystallises from dilute alcohol in thin, golden-yellow leaflets, which melt with decomposition and evolution of gas at  $239$ — $240^{\circ}$ . By the action of equal parts of the base and of phenylthiocarbimide, *methylgranatylphenylthiocarbamide*,  $C_9H_{18}N \cdot NH \cdot CS \cdot NHPh$ , is obtained; it crystallises from ethylic acetate in compact, colourless prisms which melt with previous softening at  $132$ — $133^{\circ}$ , and are soluble in methylic or ethylic alcohol or in acetone, but insoluble in water.

When methylgranatonine oxime is reduced by sodium and amylie alcohol, *ψ-methylgranatylamine* is obtained as a dense, colourless oil boiling at  $232$ — $236^{\circ}$  at the ordinary pressure; it is soluble in water, has an intense alkaline reaction, and absorbs carbonic anhydride, yielding a crystalline *carbamate* melting at about  $123^{\circ}$ . The *aurichloride*,  $C_9H_{18}N_2 \cdot 2HAuCl_4$ , crystallises from dilute hydrochloric acid in yellow needles melting with incipient decomposition at  $231$ — $232^{\circ}$ ; the *platinochloride* separates from dilute hydrochloric acid in bundles of needles melting and decomposing at  $265^{\circ}$ . The *picrate* forms a microcrystalline powder which melts with strong decomposition at  $239$ — $240^{\circ}$ . *ψ-Methylgranatylphenylthiocarbamide*,  $C_{16}H_{23}N_3S$ , crystallises from ethylic acetate in very slender, colourless needles which melt at  $176^{\circ}$  and are insoluble in water.

When boiled for a long time with a 30 per cent. caustic soda solution, or with an amylie alcoholic solution of sodium amyloxide, methylgranatylamine is transformed into the *ψ*-compound.

The relations between these two methylgranatylamines are the same as those existing between the two tropanylamine obtained by Willstätter and Müller (*Abstr.*, 1898, i, 492). T. H. P.

**β-Morphimethine.** By EDUARD VONGERICHTEN (*Ber.*, 1899, 32, 2379—2380).—The acetate of a tertiary base, *β-morphimethine*, is

obtained on adding ammonia to the filtrate from the non-nitrogenous decomposition products formed when diacetylmorphol is prepared by the action of acetic anhydride on morphinemethylhydroxide (this vol., i, 649). The *hydrochloride*,  $C_{18}H_{21}O_3N \cdot HCl + H_2O$ , prepared by hydrolysing the acetate with dilute hydrochloric acid, separates in white needles, dissolves readily in cold water and in methylic or ethylic alcohol; concentrated sulphuric acid dissolves it, forming a cherry-red solution which becomes blue when heated or moderately diluted, but intensely green if very largely diluted.

Soda produces no precipitate when added to an aqueous solution of the hydrochloride, but there results a bluish-green fluorescence resembling that of an alkaline solution of morphenol. Ammonia liberates the base in the form of a greenish, flocculent precipitate insoluble in ether, and by adding sodium methoxide in calculated amount to an alcoholic solution of the hydrochloride, the base is obtained as a brown syrup, which ultimately crystallises on treatment with ether. A *methiodide* is readily obtained, which is insoluble in absolute alcohol, but readily soluble in water; the derived ammonium base is not so unstable as the corresponding compound of  $\beta$ -methylmorphimethine.

When morphimethine hydrochloride is heated with an alcoholic solution of sodium methoxide and methylic iodide, the methiodide of  $\beta$ -methylmorphimethine is obtained. A. L.

**Alkaloids from Yohimbehe Bark.** By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1899, 23, 59—60 and 81—82. Compare *ibid.*, 1896, 20, 970, and 1897, 21, 833; and Thoms, *Abstr.*, 1898, i, 455).—Yohimbehe bark contains a dye and two alkaloids, *yohimbine* and *yohimbinine*. Yohimbine,  $C_{23}H_{32}O_4N_2$  or  $C_{22}H_{30}O_4N_2$ , is a tertiary base and crystallises from dilute alcohol in glistening, white needles, and is readily soluble in alcohol, ether, chloroform, acetone, &c., but only sparingly in water. Its specific rotatory power in alcoholic solution is  $[\alpha]_D 50.9^\circ$ . When heated at  $120$ — $130^\circ$ , or when dissolved in absolute alcohol and evaporated to dryness, it appears to be converted into the anhydroform,  $C_{23}H_{30}O_3N_2$  or  $C_{22}H_{28}O_3N_2$ .

The *hydrochloride*,  $C_{23}H_{30}O_3N_2 \cdot HCl$  or  $C_{22}H_{28}O_3N_2 \cdot HCl$ , is the only salt which has been obtained in a crystalline form; it melts at  $295$ — $300^\circ$ , but at the same time undergoes decomposition.

The *methiodide* is readily soluble in hot water, but only sparingly in cold; it is usually deposited as a syrup which slowly crystallises. An acetyl derivative melting at  $133^\circ$  has been prepared and the action of hydrochloric, hydriodic, and nitric acids on the alkaloid has been studied, but no definite products have been obtained. Oxidation with potassium dichromate and sulphuric acid yields carbonic anhydride and formic acid, whilst potassium permanganate in alkaline solution gives a small quantity of an *acid* melting at  $85^\circ$  and soluble in ether, and two acids insoluble in ether; the one, *yohimbic acid*,  $C_{20}H_{24}O_6N_2$ , is soluble, and the other, *noryohimbic acid*,  $C_{19}H_{20}O_7N_2$ , insoluble in cold alcohol. Although the alkaloid probably contains the aldehydo-group, it was found impossible to obtain an oxime or phenylhydrazone.



Yohimbine has not been obtained as yet in a state of purity; it can be freed from yohimbine by repeated solution in ethylic acetate, from which the latter crystallises, whilst yohimbine remains in solution. It may be further purified by conversion into its hydriodide, but is still probably not homogeneous, since different specimens have very different melting points. Yohimbine yields a reduction product crystallising in glistening needles and decomposing at 106—108°.

J. J. S.

**Pectin from the Fruit of the Wild-Rose.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1899, [vi], 10, 5—10. Compare this vol., i, 652).—The pectin was obtained from the cynorrhodons or fruit of the wild-rose (*Rosa canina*), either by maceration with water and precipitation with alcohol, or by treatment in an autoclave heated to 110°. It forms a light yellow powder which is entirely soluble in water. Its solutions are dextrorotatory,  $[\alpha]_D + 165^\circ$ , and, like those of other pectins, are coagulated by pectase, lime-water, baryta-water, caustic soda followed by hydrochloric acid, or by neutral or basic lead acetate. A precipitate is formed when its solution is saturated with magnesium or ammonium sulphate, and with ferric chloride the precipitate produced is coloured greenish-black, due to the presence of a tannin-like substance. When pectinase is added to an aqueous solution of the pectin, reducing substances are produced, and the solution is no longer coagulated by pectase. When the coagulum obtained by adding pectase to a solution of the pectin is treated with pectinase, it almost entirely dissolves, and reducing substances are produced.

H. R. LE S.

**Action of Heat on Pepsin.** By V. HARLAY (*J. Pharm.*, 1899, [vi], 10, 105—108).—When pepsin, dried at 50°, is heated at 100° for 3½ hours, its digestive action is not changed, but its digestive power is, perhaps, slightly diminished. This confirms the statements of Schmidt (*Centr. med. Wiss.*, 1876, 29) and Salkowski (*Virchow's Archiv.*, 1880, 81, 552). The activity of an aqueous solution of pepsin is diminished by heating it at 60° for half an hour, and the enzyme is destroyed at about 68°.

H. R. LE S.

**Action of Heat on Trypsin.** By V. HARLAY (*J. Pharm.*, 1899, [vi], 10, 166—169).—The digestive power and digestive action of dry pancreatin are in no way diminished or modified by heating it at 100° for 3½ hours (compare Schmidt, *Centr. med. Wiss.*, 1876, 29; Salkowski, *Virchow's Archiv.*, 1877, 70, 158). Its aqueous solution, however, partly loses its digestive power when heated at 55° for 1½ hours, and the enzyme is destroyed at a temperature of about 60°.

H. R. LE S.

**Invertin.** By W. A. OSBORNE (*Chem. News*, 1899, 79, 277—280).—Invertin was prepared from yeast by extraction with 96 per cent. alcohol; the solution was evaporated, and the residue again extracted with chloroform water for six days at 35°. The mixture was ultimately filtered and the filtrate dropped into 96 per cent. alcohol. The precipitated invertin was washed once with absolute alcohol and dried in a vacuum over sulphuric acid; it still contained about 50 per cent of inorganic admixture, consisting chiefly of potassium and

magnesium phosphates. For details of the methods of purification, the original must be consulted. The final product was an extremely light powder of whitish-grey colour, readily soluble in water and having invertive power of a high order and, by the lowest determination, 1.83 per cent. of ash. Various analyses indicate the average percentage composition of invertin to be C 44.54; H 6.52; N 6.1. The low percentage of carbon places invertin apart from the proteids; moreover, it gives negative results with the majority of reagents for detecting proteids; it, however, reacts faintly with copper sulphate, Millon's reagent, and the biuret test, and more decisively with lead acetate, alcohol, phosphotungstic and phosphomolybdic acids, and the xanthoprotein test. There is a suggested resemblance to chitin, inasmuch as the analytical numbers are not very different, and after boiling for a few minutes with strong or slightly dilute hydrochloric acid, invertin yields a reducing solution which, when treated with phenylhydrazine, gave a compound having the composition of phenylglucosazone, but melting at 198° instead of 205°. D. A. L.

**Composition of Albumin of the Carob Seed** (*Ceratonia Siliqua*). By ÉMILE BOURQUELOT and HENRI HERISSEY (*Compt. rend.*, 1899, 129, 391—393. Compare this vol., i, 839).—The results of further investigation of the products of hydrolysis of Carob seeds with 3 per cent. sulphuric acid at 110° prove that mannose and galactose are the only sugars formed, the product consisting of 83.5 per cent. of mannose and 16.5 per cent. of galactose.

When hydrolysed as above, 1/8 to 1/7 of the albumin taken is not acted on; this residue, on treatment with a cold mixture of sulphuric acid and water (3:1), after diluting largely and boiling for two hours, yields a sugar which consists almost entirely of mannose, and from which galactose is absent.

The mannose and galactose are present in the albumin as anhydrides of mannose and of galactose (mannans and galactans), the greater part of the former and the whole of the latter being present as hemicellulose. H. R. LE S.

**Sugar from Albumin.** By FRIEDRICH MÜLLER and JOHN SEEMANN (*Chem. Centr.*, 1899, i, 1130; from *Deutsch. med. Woch.*, 25, 209—211).—The sugar formed from albumin in diabetes does not exist preformed in the albumin molecule, but is produced from the atomic complexes containing nitrogen by a process of oxidation with elimination of nitrogen. Seemann is stated to have prepared a hexose from albumin identical with Ledderhose's glucosamine before Blumenthal and Mayer did so (this vol., i, 465, 787). E. W. W.

**Sugar from Albumin.** By FERDINAND BLUMENTHAL and PAUL MAYER (*Chem. Centr.*, 1899, i, 1131; from *Deutsch. med. Woch.*, 25, 211. Compare preceding abstract).—A reply to Müller and Seemann's claim for priority. E. W. W.

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# JOURNAL

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## THE CHEMICAL SOCIETY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

### PART II.

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#### General and Physical Chemistry.

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**Relation between Luminous Energy and Chemical Energy.**  
By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 127, 143—160).  
—Attention is drawn to the fundamental distinction which exists between endothermic photochemical reactions, in which luminous energy is transformed into chemical energy, and those exothermic reactions in which the light acts merely as an auxiliary agent, the principal part of the change being accomplished by purely chemical agencies. The former class of reactions alone is adapted for the measurement of luminous energy. In this connection, the author has studied the behaviour of a number of substances when exposed to direct sunlight or to diffused daylight, and when placed in the dark. The substances were contained in sealed tubes, and in some cases, by surrounding them with coloured media, the effects due to different radiations were distinguished.

*Nitric Acid.*—The decomposition of concentrated nitric acid by the action of light at the ordinary temperature is similar to that which takes place in the dark, at 100°, and possibly at lower temperatures, the sole products being nitric peroxide, water, and oxygen. The reaction is caused principally by the blue, or so-called chemical, rays; it is endothermic and not reversible or, at least, not entirely so. The diluted acid is not affected by light, and acid of sp. gr. 1·365, corresponding with the composition  $\text{HNO}_3 + 2\frac{1}{2}\text{H}_2\text{O}$ , was found to have undergone no appreciable amount of decomposition after several weeks exposure. At this point, a state of equilibrium is reached between the forces due

to luminous and chemical energies respectively. It is also to be noted that the nitric peroxide produced in the decomposition tends to absorb those radiations which were instrumental in its formation.

*Iodic Acid.*—Both iodic acid and iodic anhydride are stable in diffused light at the ordinary temperature, but are decomposed by direct sunlight with liberation of iodine and oxygen. The decomposition is analogous to that which is brought about by heat alone at about  $300^{\circ}$ , and is limited by the absorptive action of the iodine vapour and by the deposition of solid iodine on the surface of the compound. For this reason, the reaction, although accompanied by the absorption of a considerable amount of heat, is unsuitable for the measurement of luminous energy.

*Hydrogen Iodide.*—The decomposition of hydrogen iodide lies on the border line of exothermic and endothermic reactions, but the author inclines to the conclusion that it is accompanied by the development of heat =  $0.4$  Cal. If solid iodine separates, the reaction is undoubtedly exothermic (+  $6.4$  Cal.). The decomposition is due to the blue and violet rays and takes place slowly in diffused light, more quickly in direct sunlight, with the intermediate formation of hydrogen periodide ( $\text{HI}_3$ ?). Aqueous solutions of hydrogen iodide are not decomposed by direct sunlight, unless air or oxygen is present.

*Hydrogen Bromide.*—Gaseous hydrogen bromide is not affected by the action of light, even at  $100^{\circ}$ . This fact is in accordance with the observation, previously recorded, that the action of light accelerates the decomposition of water by bromine.

*Various Gaseous Mixtures.*—No action was observed in the case of the following systems when exposed to light, either in the dry or moist state:  $\text{CO}_2 + 2\text{H}_2$ ;  $\text{CO}_2$ ;  $\text{CO} + 2\text{H}_2$ ;  $\text{CO}$ ;  $\text{SO}_2 + 3\text{H}_2$ ;  $\text{HNO}_3 + \text{H}_2$ ;  $\text{CO} + 8\text{O}_2$ ;  $\text{CO} + \text{O}$ ;  $\text{CO} + \text{air}$ .

*Metallic Oxides and Salts.*—Red mercuric oxide undergoes decomposition more rapidly than the yellow modification, and the action is, in each case, much increased by the presence of moisture. Mercurous oxide, when exposed to light, yields a small quantity of metallic mercury and becomes yellow in parts, but no gas is evolved. No action was observed in the case of lead peroxide, silver oxide, and mercuric chloride, bromide, and iodide. Mercuric and mercurous acetates, exposed in vacuous tubes, blacken on the surface and evolve a little carbonic anhydride, especially when moist. These reactions, however, are exothermic and caused by the oxidising action of the salts.

*Silver Haloids.*—The decompositions which may occur are endothermic, both in the presence and absence of moisture. Since, however, the reactions are reversible, they are not suited for photochemical measurements.

According to these observations, the measurement of luminous energy by transformation into chemical energy is to be effected by means of endothermic reactions which are irreversible at the ordinary temperature. In order that the results may be additive, or proportional to the time of exposure, it is necessary to employ fluid systems admitting of uniform action throughout their mass. In any case, the chemical effect is a measure only of the particular radiations, varying for each substance, which are actually absorbed. In comparing the chemical effects of light and heat, it is pointed out that all decompositions may be effected

by means of heat, whereas the action of light, and, usually, of particular radiations, only brings about certain reactions. N. L.

**Influence of Association of Liquids on their Optical Activity.** By L. TSCHUGAEFF (*Ber.*, 1898, 31, 2451—2454).—The optical activities and molecular volumes of four organic salts of menthol were determined, with the object of testing the validity of Crompton's views as to the relationship subsisting between the association and optical activity of organic liquids. The numbers obtained were as follows, where  $V_T$  = calculated molecular volume, and  $V_E$  = molecular volume observed.

	$d\ 20^\circ/4^\circ$	$V_T$	$V_E$	$V_E - V_T$	$[M]_D$
Phenylacetate . .	0.9874	271.4	277.5	+6.1	-190.7
Phenylpropionate	0.9851	287.5	292.4	4.9	-161.9
Metatoluate ... ..	0.9931	271.4	275.9	4.5	-241.0
Orthotoluate . .	0.9972	271.4	274.7	3.3	-231.3

It is clear that there is here no reason to assume association, and, whilst the difference between the calculated and observed molecular volumes of the phenylpropionate and metatoluate are practically identical, their molecular rotations are entirely different. It cannot be supposed, therefore, that the molecular rotations of the two liquids are dependent on their degrees of association.

Similar results have been obtained by Frankland and McCrae in the case of the ethereal salts of tartaric acid (*Trans.*, 1898, 307). It seems probable, therefore, that the state of association of a liquid does not exercise a predominating influence on its optical activity.

Additional evidence is cited, showing the insufficiency of Crompton's view. Thus amylic alcohol is lævorotatory, whilst its ethereal salts are dextrorotatory, to an amount which at first increases with rise in the homologous series, and finally becomes constant. This, according to Crompton's view, is the result of decrease in the degree of association, which begins with the free alcohol and culminates in the salts with constant rotation; it would be expected, therefore, that any cause which lessens the state of association of the alcohol should alter its rotation in the sense of approaching that of the higher alkylic salts. It has been shown by Guye and Aston, however (*Abstr.*, 1898, ii, 469), that amylic alcohol in the state of vapour or in dilute solution has a more powerful lævorotation than when in the state of liquid at a low temperature; and since the molecular weight, as determined by static and cryoscopic methods, has a normal value, association is excluded, and its disappearance has an effect opposite to that anticipated by Crompton's theory. A. L.

**Compound Line-spectrum of Hydrogen.** By R. S. HUTTON (*Phil. Mag.*, 1898, [v], 46, 338—343).—The author's results support the generally accepted conclusions that the compound line-spectrum of hydrogen is a true hydrogen spectrum, and render it probable that the disappearance of the compound line-spectrum in vacuum tubes that have been previously washed out by oxygen, as observed by Cornu, may be explained by the fact that traces of oxygen remained in the tube, such traces almost completely destroying the compound spectrum. H. C.

**Appearance of the Cleveite and other new Gas Lines in the Hottest Stars.** By SIR J. NORMAN LOCKYER (*Proc. Roy. Soc.*, 1897, 62, 52—67. Compare Abstr., 1898, ii, 2).—This paper continues the discussion of the value of the relative intensities of certain lines in the spectra of stars as criteria of their relative temperatures, with special reference to those stars near the apex of the temperature curve. The relative behaviour of certain lines as the temperature increases or decreases is deduced by direct comparison of the spectra of some typical stars, as by this means an indication is obtained as to which lines are intensified and which thin out as the temperature changes, and thus affords a basis for the determination of the sequence of the hottest stars.

It is shown that, of the Cleveite gas lines (1) the gas *X* does not vary absolutely with helium; (2) gas *X* varies its intensity at a rate different from that of helium; (3) although helium and gas *X* reach their maxima nearly together, the maximum of gas *X* is short lived, whilst that of helium is prolonged. These facts indicate that helium and gas *X* are to be regarded as distinct substances.

A comparison of the principal and subordinate series of lines makes it clear that, in tracing the progress of gas *X* through the stars of increasing and decreasing temperature, the lines of the principal series, as tabulated in the laboratory, become of secondary importance; the first subordinate series becomes pre-eminent in intensity, and the second subordinate series almost entirely disappears, near the point of maximum temperature. In the case of gas *X*, as the principal series is not intensified to the same extent as the first subordinate series in passing from Rigel to Bellatrix, it is suggested that perhaps the molecules corresponding with the former series do not survive the higher temperatures. It is thought that as yet there is no reason to regard the three series of gas *X* or helium as representing different constituents, but three sets of molecules of different complexities. In view of the definite nature of the results which have been obtained, the author thinks that gas *X* should now be distinguished by a definite name, and suggests "asterium" as the most suitable.

In view of the probable existence of other new gases in the hottest stars, it becomes of importance to have a means of discriminating between gaseous and metallic lines. It is fair to assume that, in the nebulae, the unknown bright lines will belong to gases, as in them the lines of hydrogen, helium, and asterium are found, but no indication of the enhanced lines of Fe, Mg, Mn, Si, &c., the existence of a moderately low temperature being thus indicated. Again, in  $\alpha$ -Cygni, where the enhanced metallic lines are strong, the helium lines are once more strongly developed; hence the lines of gases which behave like helium in stars as well as nebulae may be expected to be intensified in passing from  $\alpha$ -Cygni through successively hotter stars. A table of lines behaving in this manner is given; these are  $\lambda = 3912\cdot2, 3994\cdot7, 4040\cdot6, 4069\cdot7, 4071\cdot7, 4075\cdot7, 4088\cdot7, 4094\cdot7, 4104\cdot8, 4114\cdot8, 4172\cdot6, 4253\cdot6, 4267\cdot6, 4314\cdot6, 4345\cdot6, 4415\cdot2, 4541\cdot8, 4566\cdot8, 4574\cdot8, 4613\cdot8, 4643\cdot8, 4650\cdot9$ .

From a list of new lines observed by the author with gases from terrestrial sources, he extracts the following, which probably have

counterparts in the hotter stars:  $\lambda = 3929\cdot4, 3961\cdot6, 4002\cdot9, 4069\cdot7, 4072\cdot2, 4114\cdot6, 4309\cdot4, 4338\cdot0$ . The lines observed in the spectra of gases from minerals may be divided into two groups, the first comprising those which are strong in  $\alpha$ -Cygni, and diminish at higher temperatures, and the second, those which are absent or weak in  $\alpha$ -Cygni, and become stronger with higher temperature. The lines of the first group behave like the enhanced lines of the metals, and at present it is impossible to say whether the corresponding stellar lines are produced by gases or are an accidental coincidence; in the case of the second group, however, there is much probability that they represent new gas lines.

A minute examination of the spectrum of Bellatrix has been made by Dr. W. J. S. Lockyer, with a view of ascertaining whether some of the still unknown lines might form a series. Fifty unknown lines are left after eliminating those due to hydrogen, helium, and asterium, and it is probable that two series are present, but the question awaits better photographs of the spectrum.

A comparison of the spectra of  $\zeta$  Puppis, as given by Pickering (*Astrophysical Journal*, 4, 369), and of Bellatrix proves that they only differ markedly in the presence of those new lines in  $\zeta$  Puppis which Pickering showed were computable from the formula representing the hydrogen spectrum using odd values of  $n$  instead of even. On the supposition that this new series of probable hydrogen lines was due to a transcendental temperature, attempts have been made to produce them, by means of high tension sparks in hydrogen, but without success.

In conclusion, the author's preliminary investigations have shown that, with increasing temperature, hydrogen is first visible, then helium and asterium appear nearly together, and, finally, unknown lines at wave-lengths 4088·7 and 4650·9, these last two being at a maximum when the lines of asterium have considerably decreased. It is still doubtful, however, whether Bellatrix on the one hand, or  $\epsilon$  Orionis and  $\zeta$  Puppis on the other, may be taken as typical of the hottest stars.

A. L.

**A Third Class of Electrode.** By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1897, 28, 364—366).—A form of cell is designed in which there is obtained a reversible electrode of a metal which decomposes water, as, for example, the following—Lead in a mixture of calcium and lead sulphates in a solution of a calcium salt. In this case, the potential difference at the electrode is  $\pi = K \log. k_2/(Pb'')$ , but  $(Pb'') \times (SO''_4) = k_1$  and  $(Ca'') \times (SO''_4) = k_2$ , hence  $\pi = K \log. k_3/(Ca'')$ . The availability of such a form of electrode is proved by the determination of the E. M. F. of chains containing such electrodes of zinc with those containing ordinary electrodes; the values only differed by 0·001 volt. It is evident that the salts employed must be only slightly soluble, and must form no double compounds or mixed crystals.

L. M. J.

**Electrical Oscillations.** By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Zeit. physikal. Chem.*, 1898, 27, 343—344). (See Kauffmann, Abstr., 1898, ii, 550).—The authors had also found that characteristic spectra are produced by electrical discharges in organic compounds, and give the position of the limits and maximum in-

tensity of the spectra given by a number of compounds of naphthalene, anthracene, &c. (Abstr., 1896, ii, 86). L. M. J.

**Method for Determining the Resistance of Electrolytes.** By PARKER C. McILHINEY (*J. Amer. Chem. Soc.*, 1898, 20, 206—209).—The method described, whilst not so accurate as that of Kohlrausch, is of advantage for making many readings in a short space of time. It consists in determining by a galvanometer, preferably a d'Arsonval, the potential difference between the ends of a known resistance placed in series with the resistance to be determined. The current is supplied by a gravity battery, and before passing through the electrolyte it is transformed into an alternating current by means of a rotatory pole changer, but the current passing through the known resistance is direct. When a current passes through two resistances in series, the fall of potential in each of them is proportional to its resistance. H. C.

**Electrical Conductivity in Mixed Salt Solutions.** By H. HOFFMEISTER (*Zeit. physikal. Chem.*, 1898, 27, 345—353).—The quantity of an ion which passes across a section of the electrolyte is a function of the conductivity, valency, current strength, concentration, and ion velocity, and hence by determination of the increase of concentration of an ion in the anode or cathode liquid the actual concentration of the ions may be determined if the velocity is known. The author has in this manner determined the concentration of the silver and hydrogen ions in mixed solutions of silver nitrate and nitric acid, and compared the results with those calculated on an assumption of Rudolphi's dilution law. Similar experiments were performed with sodium acetate and acetic acid; in this case, owing to the slight dissociation of acetic acid, its addition has but little effect on the concentration of the sodium ions.

NOTE ON ABOVE BY HANS JAHN.—The above method affords a means of testing the validity of the dilution law which assumes that the ion velocity is not a function of the concentration. Some unpublished experiments indicate the connection  $uC\sqrt{V} = \text{constant}$  where  $u$  is the ion velocity,  $C$  the concentration, and  $V$  the volume in which 1 gram molecule is dissolved. L. M. J.

**Physico-chemical Investigation of Diazonium Salts, Diazonium Hydroxide, and Normal Diazotates.** By WILLIAM B. DAVIDSON and ARTHUR HANTZSCH (*Ber.*, 1898, 31, 1612—1648).—In a previous paper (Abstr., 1895, ii, 516), it has been shown by one of the authors that the diazonium radicle,  $\text{PhN:N}$ , is strictly analogous to the ammonium radicle in its salt forming properties, and that diazonium must be regarded as a fully substituted ammonium of the quaternary type. This appears also from the investigation of the conductivity of the salts and the hydroxide. The temperature coefficients are found to accord with Arrhenius' rule for normal salts, salts of the smaller conductivity having the higher temperature coefficients. The molecular conductivity increases with the dilution exactly as in the case of potassium or ammonium salts. The rate of migration of the diazonium ion at  $25^\circ$ ,  $\alpha = 45.7$ , compares with that



given by the quaternary bases pyridinemethylum,  $\alpha = 44.3$ , and tetramethylammonium,  $\alpha = 43.6$ , but differs entirely from that of the primary phenylammonium,  $\text{Ph} \cdot \text{NH}_2$ . The affinity constant of diazonium hydroxide at  $0^\circ$  is approximately 0.123, which is nearly 70 times greater than that of ammonium hydroxide, and even greater than that of piperidinium hydroxide. The rate of saponification of diazonium hydroxide at  $0^\circ$  and  $v = 128$  is about one-half that of sodium hydroxide. From the rate of saponification, diazonium hydroxide would contain at  $0^\circ$  and  $v = 128$  about 43 per cent. of hydroxyl ions; the number obtained from the conductivity is about 33 per cent. Hence diazonium hydroxide would appear to be about one-third dissociated in solutions of this concentration.

In the undissociated state, the diazonium hydroxide is present chiefly in the form  $\text{OH} \cdot \text{NPh} \cdot \text{NH} \cdot \text{OH}$  intermediate between the true diazonium and the syn-diazo-hydroxide. This would appear from the acid character of the solutions of diazonium hydroxide, a definite heat of neutralisation with sodium hydroxide being observed exactly as in the case of an acid. This is fully explained by the oxime-like structure of the syn-diazo-hydroxide. The syn-diazotates undergo hydrolysis to a remarkable and abnormal extent in dilute solution, the hydrolysis increasing more rapidly with the dilution than is the case with other salts decomposed by water. This is probably due to the formation of the intermediate compound already alluded to and the transformation of this into diazonium hydroxide.

H. C.

**A New Fixed Point in Thermometry. A Proposal for a Normal Room Temperature.** By WILHELM MEYERHOFFER and A. P. SAUNDERS (*Zeit. physikal. Chem.*, 1898, 27, 367—368).—The transition point of a mixture of sodium chloride and sodium sulphate in molecular proportion is  $17.9^\circ$ , and is thus approximately the ordinary room temperature. The advantages claimed by Richards for the transition point of sodium sulphate as a fixed point hold also in this case, and the authors suggest that it might be employed for a normal room temperature (*Abstr.*, 1898, ii, 555).

L. M. J.

**Latent Heat of Evaporation of Zinc and Cadmium.** By WILLIAM SUTHERLAND (*Phil. Mag.*, 1898, [v], 46, 345—346).—The usual thermodynamical equation for the latent heat of evaporation of a gram of liquid at absolute temperature  $\theta$  and of volume  $v_1$  into saturated vapour of volume  $v_3$  at saturation pressure  $p$ ,  $\lambda = \theta \frac{dp}{d\theta} (v_3 - v_1) / J$ ,

has been so thoroughly verified that it furnishes an experimental method of determining  $\lambda$  without the necessity of direct calorimetric measurements. From the relation between  $p$  and  $\theta$  for zinc and cadmium determined by Barus, the author calculates the heats of vaporisation of gram-molecules of these metals as liquids, in kilocalories 28.3 for zinc and 29.6 for cadmium.

H. C.

**Freezing Point of Aqueous Solutions of Sodium Mellitate.** By W. W. TAYLOR (*Zeit. physikal. Chem.*, 1898, 27, 361—363).—The molecular depression of the freezing point was determined for various solutions of the above salt which, for complete dissociation, should form seven ions. The most dilute solutions (0.0018 gram-mols,

per litre) gave a depression of  $5.92 \times 1.87^\circ$ , and the most concentrated (0.277 gram-mols. per litre)  $3.77 \times 1.87^\circ$ . L. M. J.

**Cryoscopic Behaviour of the Picrates.** By GIUSEPPE BRUNI and R. CARPENÉ (*Gazzetta*, 1898, 28, ii, 71—83).—The authors have examined the cryoscopic behaviour of the picrates of naphthalene, phenanthrene, anthracene,  $\alpha$ - and  $\beta$ -naphthol, phenylcoumalin,  $\alpha$ -naphthylamine, 2'-methylindole, 2':3'-dimethylindole, 2'-methyl-3'-ethylindole, carbazole, 2'-methyl-dihydroindole,  $\alpha\beta\beta$ -trimethylindolenine,  $n\beta\beta$ -trimethyl- $\alpha$ -methyleneindoline,  $n\beta\beta$ -triethyl- $\alpha$ -methyleneindoline,  $\beta\beta$ -diethyl- $\alpha$ -methylindoline, 2':4'-dimethylquinoline, and pseudopelletierine, using acetophenone as the solvent.

The picrates of the hydrocarbons, phenols, and lactones are completely dissociated in acetophenone solution; those of the indoles and carbazoles are wholly dissociated in dilute solution, but not in more concentrated ones. No sharply defined differences in cryoscopic behaviour distinguish additive compounds of picric acid from the picrates of organic bases; the degree of dissociation diminishes as the basicity of the base increases. W. J. P.

**New Method of Determining the Vapour Pressures of Solutions.** By E. B. H. WADE (*Proc. Roy. Soc.*, 1898, 62, 376—385).—A detailed description of the apparatus employed by the author in carrying out the determinations recorded in a previous paper (see Abstr., 1898, ii, 15). H. C.

**Vapour Pressure of Hydrated Crystals.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1898, 27, 323—336).—Andr  has shown that the vapour pressure of hydrated salts is, between wide limits, independent of the water content, and changes suddenly at points corresponding with definite hydrates (Abstr., 1891, 981). In cases of incomplete equilibrium, however, the vapour pressure may change continuously with the removal of water, and this occurs for all the compounds examined by the author, which are all hydrated silicates, namely gmelinite, phacolite, chabazite, leonhardite, saumontite, phillipsite, gismondine, okenite, natrolite, scolesite, pyrophyllite, thomsonite, prehnite, uranite, and hyalite, and curves of vapour pressure against water concentration are given. The change of hydration is usually reversible, but if the dehydration is carried on until the pressure falls below about 1 mm., the hydration does not again reach its original value. L. M. J.

**Dehydration of Crystalline Salts.** By THEODORE W. RICHARDS (*Zeit. anal. Chem.*, 1898, 37, 583—584, from *Proc. Amer. Acad. Arts and Sci.*, 33, 23).—In a desiccator containing phosphoric anhydride, crystals of barium chloride lose one molecule of water rapidly, but the second molecule more slowly. Most salts which crystallise with a small number of molecules of water behave similarly, but those with a large amount of water of crystallisation give it up in a gradual and continuous manner. It is, however, suggested that, by employing dehydrating agents of lower hygroscopic character, the different tensions of the individual water molecules might be recognised by the rate at which loss of weight proceeded. M. J. S.

**Velocity of Diffusion of Gases through Water and through Agar Jelly.** By GUSTAV HÜFNER (*Zeit. physikal. Chem.*, 1898, 27, 227—249).—Exner's rule, that the velocities of diffusion of gases through water are inversely proportional to their densities, is not obeyed by hydrogen and ammonia when referred to carbonic anhydride, whilst the agreement in the cases of oxygen and nitrogen is only apparent (Abstr., 1897, ii, 249), as the temperature of observation was different for the two latter gasses. The velocity of diffusion of ammonia was, therefore, determined with the aid of a hydrophane division as explained in the previous paper (*loc. cit.*). The values obtained were,  $k_0 = 0.727$ ;  $k_5 = 0.822$ ,  $k_{10} = 0.953$ ,  $k_{15} = 1.106$  and  $k_{20} = 1.250$ . These results, although totally different from those of Müller, agree well with those of Voigtländer (Abstr., 1889, 817) for the diffusion in agar jelly. The value is, however, only one-half that calculated from the diffusion velocity of carbonic anhydride by means of Exner's law, and thus indicates a double molecule. The diffusion velocity of hydrogen in agar jelly was found to be  $k_{10} = 3.75$ , which is in accord with the values found by the hydrophane method,  $k_{16} = 4.09$ ,  $k_{21} = 4.45$ . Assuming the influence of temperature to be given by the expression  $k_t = k_0(1 + at)^2$  the coefficient  $a$  was found to be 0.010295 in the case of carbonic anhydride. From the diffusion velocity of the latter, those of a number of acids, salts, and bases are calculated, but the values so found do not agree with the determinations of Voigtländer. In the case of the alkali hydroxides, the velocity increases with the molecular weight. The author also calculates the association necessary to give values in accord with the determinations, and finds that, in formic acid, three molecules, in acetic acid, five molecules, and in butyric acid seven molecules are associated. L. M. J.

NOTE.—The diffusion of an undissociable compound cannot, however, be legitimately compared with that of an electrolyte, so that deductions drawn from such a comparison are invalid. L. M. J.

**Osmotic Pressure.** By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1898, 20, 579—585).—When a solution and the pure solvent are separated by a semi-permeable diaphragm, at equilibrium the counter pressure preventing the entrance of the solvent into the solution, is commonly given as equal to  $hs$  on the unit surface,  $h$  being the height of the column of liquid and  $s$  the density of the solution whose counter pressure balances the osmotic pressure. The author argues that, as the diaphragm receives the full pressure of the solute, the hydrostatic pressure which prevents the entrance of the solvent comes only from the column of pure solvent in the solution, and that the quantity  $s$  given above should apply to the pure solvent and not to the solution. H. C.

**Solubility of Mixed Electrolytes of Two Ions containing no Common Ion.** By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1898, 27, 267—278).—For the complete determination of the solubility of a salt  $C.D.$  in a solution of  $A.B.$  of known concentration, the solution of nine equations containing nine unknown quantities is necessary. This, although possible, is extremely tedious, and the author, therefore, shows how the determination may be simplified very greatly. Three

cases occur, (1) where both secondary compounds, that is, *B.C.* and *A.D.*, are highly dissociated, (2) where one of these compounds and *C.D.* are highly dissociated, and (3) where only one of the secondary compounds is highly dissociated. The accuracy of the expressions are proved in the several cases by solubility determinations for a mixture of (1) thallium chloride and potassium nitrate, (2) silver benzoate and nitric acid, (3) silver benzoate in monochloroacetic acid. L. M. J.

**Solubility of Salts of a Weak Acid in a Strong Acid.** By ARTHUR A. NOYES and DAVID SCHWARTZ (*Zeit. physikal. Chem.*, 1898, 27, 279—284).—The experiments were made in order to test the validity of the expressions deduced by Noyes (preceding abstract). Silver benzoate was dissolved in solutions of nitric and chloroacetic acids of various concentrations and the values found compared with those calculated by Noyes' expressions. The general accord of the result is seen from the following examples.

Nitric acid.			Chloroacetic acid.		
Concentration.	Sol. found.	Sol. calc.	Concentration.	Sol. found.	Sol. calc.
0.004435	0.01395	0.01406	0.0000	0.01144	—
0.008915	0.01715	0.01706	0.003935	0.01385	0.01386
0.01783	0.02351	0.02396	0.00787	0.01612	0.01588
0.02674	0.03071	0.03159	0.01574	0.02093	0.02117

L. M. J.

**Aqueous Solutions of two Salts with one Common Ion. II.** By C. HOITSEMA (*Zeit. physikal. Chem.*, 1898, 27, 312—318).—The solubility isothermals at 20° were determined for mixtures of (1) salicylic acid and sodium salicylate, (2) hippuric acid and potassium hippurate. In both these cases, a double salt occurs but no mixed crystals or complex molecules, and the solubility phenomena are in accord with the general form of curve for such a case deduced previously by the author (*Abstr.*, 1898, ii, 157). L. M. J.

**Cause of the Dissociative Power of a Solvent.** By JULIUS W. BRÜHL (*Zeit. physikal. Chem.*, 1898, 27, 319—322).—It has been shown by Cady that liquid ammonia possesses a great dissociative power, probably equal to that of water (*Abstr.*, 1898, ii, 203). Solvents of high dissociative power have also a high dielectric constant, and are usually liquids consisting of polymerised molecules. Hitherto, the dissociative power has been regarded as chiefly dependent on the existence of oxygen, and especially of hydroxyl groups, and the author considers it due to the quadrivalent nature of oxygen (*vide Abstr.*, 1897, ii, 198), which hence in water and many other compounds is unsaturated and thus causes the separation of the ions and the polymerisation of the compound. The property of passing from a lower to a higher valency is also possessed by nitrogen, and the

dissociative power of ammonia is probably due to this, it being noteworthy that many other nitrogen compounds cause dissociation, for example, the fatty nitriles, nitro-ethane, aniline, &c. (Dutoit and Aston, *Abstr.*, 1897, ii, 546). For the same reason, the author considers it probable that liquid ammonia is polymerised and has a high dielectric constant. The unsaturation is different in kind from that of doubly linked carbon, but probably liquid acetylenes would also possess dissociative power.

L. M. J.

**Validity of the Dilution Law.** Reply to Objections of Noyes. By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1898, 27, 337—342).—The objections raised by Noyes to the author's expressions (compare *Abstr.*, 1898, ii, 158) are unfounded, and Noyes' own expressions are almost identical with the author's. The validity of the deduced expressions is illustrated by a comparison of the calculated values, with those found, for the heat of dilution in the case of silver acetate, propionate, butyrate, and orthonitrobenzoate.

L. M. J.

**Solubility of Iodine in Dilute Solutions of Potassium Iodide.** By ARTHUR A. NOYES and J. SEIDENSTRAKER (*Zeit. physikal. Chem.*, 1898, 27, 357—360).—Jakowkin's experiments (*Abstr.*, 1894, ii, 271) indicate that, in its solutions in aqueous potassium iodide, the iodine is present as potassium tri-iodide, but this is not in agreement with the fact that the addition of water to the saturated solution causes a precipitation of iodine, for since the active mass of the iodine must here be constant ( $KI_3 = k(KI)$ ), and dilution should cause no precipitation as the ratio is unaltered.\* Jakowkin's results hence probably only extend to moderately dilute solutions. The authors have, therefore, determined the solubility of iodine in dilute solutions of potassium iodide and compared the quantity of assumed tri-iodide with that of remaining iodide. The ratio is approximately constant, so that for solutions from 0.1 to 0.005 N., Jakowkin's results are confirmed.

L. M. J.

\*NOTE.—This conclusion is incorrect, inasmuch as proportionality only exists between the tri-iodide and *undissociated* potassium iodide and the concentration of the latter decreases on dilution, so that precipitation may occur.

L. M. J.

**Properties of Liquid Mixtures.** By R. A. LEHFELDT (*Phil. Mag.*, 1898, [v], 46, 42—59).—The vapour pressures of mixtures of any two of the following four liquids were determined by the dynamic method: benzene, toluene, carbon tetrachloride, and alcohol. When the vapour pressures are plotted against the molecular percentages, the difference between the alcohol curves and those of the normal liquids is most marked, for whilst mixtures of carbon tetrachloride and benzene, or carbon tetrachloride and toluene, have a vapour pressure never very different from that which would be obtained by interpolation from the pressures of the pure substances, both mixtures containing alcohol show a maximum—a very flat one. In the case of alcohol and benzene, it occurs at about 40 per cent. (molecular) of alcohol, and is 406 mm., being  $406/(271 + 220) = 83$  per cent. of the sum of the pressures of the pure substances, whilst for alcohol and

toluene it is at about 74 per cent. of alcohol, and has the value, 249 mm., which is  $249/(93 + 220) = 80$  per cent. of the sum of the pressures. If  $q$  is the ratio of the masses of the two substances present in the liquid, and  $t$  is their ratio in the vapour, for normal liquids the relation  $\log t = \log k + r \log q$ , where  $k$  and  $r$  are constants, holds for mixtures which do not contain a very small proportion of either constituent. For mixtures containing alcohol, the relations between  $\log t$  and  $\log q$  are very far from linear. Linebarger's rule, that the partial pressure of benzene and toluene in mixtures is simply proportional to the molecular percentage present, is not found to hold good. H. C.

**Speed of Coagulation of Colloidal Substances.** By CHARLES E. LINEBARGER (*J. Amer. Chem. Soc.*, 1898, 20, 375—380).—Solutions of many colloids can be made to coagulate or gelatinise by the addition of a mere trace of certain substances; the striking analogy between this phenomenon and that of crystallisation has often been insisted on. If there is a true analogy, the addition of a small amount of a substance having the power to start coagulation in one part of a colloid solution should result in the spread of the coagulation at a certain rate throughout the whole solution, just as happens in the case of crystalloids in supersaturated solution. Experiments were made with colloidal ferric hydroxide, with silicic acid, and with egg-albumin which seem to prove that coagulation started in one part of a solution does not necessarily spread through the whole body of the solution. The author concludes that it is extremely improbable that colloid solutions are comparable with supersaturated solutions. H. C.

**Absorption. Formation of Colloids, and their Structure.** By JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1898, 18, 14—36. Compare Abstr., 1897, ii, 137).—The formation of a colloid is the separation of a solution into two liquids, of which the one, the hydrogel, has a greater viscosity than the other, and forms a network which retains the solution partly absorbed and partly inclosed in the interstices. The conversion of the hydrogel into a glassy or horn-like substance is a continuous process depending on various conditions, such as the influence of a third substance, time, and the evaporation of the solution. The conversion of a colloid into a colloid with another liquid, the osmotic properties, the absorption, the expulsion of liquid by pressure, the formation of interstices, the continuous manner in which the contained liquid is evaporated by the influence of temperature and vapour tension, and the evaporation of this liquid, all take place in accordance with the view that the hydrogel is a cell-like structure of network. E. C. R.

**Inflammability of Thin Layers of Explosive Gases. II.** By FRIEDRICH EMICH (*Monatsh.*, 1898, 19, 299—320. Compare Abstr., 1897, ii, 309).—The explosion tube has been altered so that it has a capacity of only a few cubic centimetres; with this apparatus, the air or the products of combustion may be completely removed in a few minutes.

With mixtures of hydrogen and chlorine, it is found that the

mixture which is most readily inflammable is that which contains only half as much hydrogen as is required for complete combustion. It has also been shown that the inflammability is practically proportional to the pressure. Mixtures of methane and of oxygen have also been investigated, the oxygen being obtained by heating potassium chlorate in a copper tube, and the methane by Gladstone-Tribe's method. The mixture which is most readily inflammable is the one containing 1 volume of methane to 3 volumes of oxygen. With mixtures of carbonic oxide and oxygen, it has been found that small quantities of water vapour have an immense influence on the inflammability of the mixture; by increasing the amount of water from 0.25 to 0.5 per cent., the inflammability increases some 300 per cent. For this reason, the experiments have been conducted with mixtures of carbonic oxide and oxygen saturated with moisture. The mixture which is most readily inflammable is that which is completely combustible, namely, 2 volumes of carbonic oxide to 1 of oxygen.

J. J. S.

**Reactions in Mixtures of Alcohol and Water.** By WLADIMIR A. KISTIAKOWSKY (*Zeit. physikal. Chem.*, 1898, 27, 250—266).—The reaction velocity for the hydrolysis of an ethereal salt in aqueous alcohol is given by the equation  $dx/dt = k(a-x) - k_1x$ , since the concentration of alcohol and water may be regarded as constant. The values of  $k$  and  $k_1$  are given by the expressions  $1/t \times x/a \times \log (X/\overline{X-x})$  and  $1/t \times (a-X)/a \times \log (X/\overline{X-x})$ , where  $X$  is the final equilibrium value of  $x$ . For the formation of the ethereal salt, the expressions are precisely similar. The values of the two constants were calculated from both the rates of formation and of decomposition of ethylic acetate and ethylic oxalate, hydrochloric acid being used as hydrolyser, and were in all cases concordant. The values are independent of the initial concentration of the organic acid, but vary considerably with the alcoholic concentration of the solvent. The velocity at first decreases with increasing percentage of alcohol, but for concentrations above 70 per cent. it again increases. For monochloracetic acid, the value  $k+k_1$  is less than that for acetic acid, and for the di- and tri-chloracetic acids no results could be obtained, the behaviour of these being closely analogous to that of inorganic acids. When an acid is used as hydrolyser, the velocity is approximately proportional to the concentration of this acid, but when none is employed, the values of  $k$  and  $k_1$  are functions of the concentration of the organic acid, and decrease rapidly with increasing percentage of alcohol.

L. M. J.

**Velocity of Hydrolysis of Alkyl Phosphates.** By JACQUES CAVALIER (*Compt. rend.*, 1898, 127, 114—115).—In studying the hydrolysis of these ethereal phosphates, the author dissolves one molecule of the salt in 10 litres of water at 88°. Under these conditions, the decomposition obeys the law for monomolecular reactions. The three methylic phosphates are hydrolysed more rapidly than the corresponding ethylic salts. When trimethylic phosphate is employed, it is found that the first methyl group is removed most rapidly, whilst

the velocity of hydrolysis of the second is least, and that of the third has an intermediate value. Similar velocities are obtained in the case of triethylic phosphate. This unexpected result does not hold for the di- and mon-allylic phosphates, for the latter is decomposed less rapidly than the former; the triallylic compound, being insoluble in water, could not be employed in these experiments. The velocity of hydrolysis varies greatly with the temperature; at  $44^{\circ}$ , it is 100 times less than at  $88^{\circ}$ .

The trialkylic salts are far more rapidly hydrolysed by bases than by water; on the other hand, the metallic salts of the di- and mon-allylic phosphates are scarcely decomposed either in alkaline or aqueous solutions even at  $90^{\circ}$ .

G. T. M.

**Chemical Equilibrium between Amalgams and Solutions.** By A. Ogg (*Zeit. physikal. Chem.*, 1898, 27, 285—311).—If mercury and an aqueous solution of silver nitrate are shaken together, equilibrium is finally attained between silver nitrate, mercurous nitrate, and the amalgam. In this case, since the concentration of the mercury is practically constant, if  $a$  is the equivalent concentration of the silver nitrate,  $b$  that of the mercurous nitrate, and  $c$  that of the silver in the amalgam, then  $a/bc = \text{constant}$ , if the mercury ions are univalent, and  $a/c\sqrt{b} = \text{constant}$ , if the ions are bivalent. The latter equilibrium equation is that which actually obtains, the constancy of the first expression found in the author's previous paper (*Abstr.*, 1897, ii, 366) being due to insufficient change in the concentration of the mercurous salt; the mercurous ions hence are  $\text{Hg}^+ - \text{Hg}$ . If sufficient silver nitrate be used, a saturated solid amalgam is formed, and the active mass of the silver becomes constant, the equilibrium equation must reduce to  $a/\sqrt{b} = \text{constant}$ , and this result was experimentally verified. The reverse equilibrium between silver and mercurous nitrate could not be attained, and it is probable that only surface amalgams are produced, even when the silver is present as a very fine powder. In the equilibrium of mercury, mercurous and mercuric nitrates, the ratio of the concentrations of the two salts is constant, a result again confirming the bivalency of the mercurous ions. This is also further established by the determination of the E. M. F. of cells consisting of two mercury electrodes in solutions of mercurous nitrate of concentration 1 : 10 respectively; the E. M. F. reduces to  $0.058/n$  volts where  $n$  is the valency of the ions, and was found to vary from 0.0265 to 0.0305. Conductivity determinations proved that dilution produces a change of dissociation equal to that produced in solutions of lead nitrate, whilst freezing point experiments also support the formula  $\text{Hg}_2(\text{NO}_3)_2$ , so that there appears but little doubt concerning the structure of mercurous salts. The solution tension of mercury is very nearly equal to that of silver, and the difference of potential between reversible electrodes of silver and mercury changes sign by dilution of the salts. The vapour pressure of amalgams containing excess of mercury is very nearly equal to that of pure mercury, but falls considerably when the composition of the amalgam reaches  $\text{Ag}_3\text{Hg}_4$ . Experiments also prove that this amalgam is in equilibrium with mercury; from the temperature coefficient of the equilibrium con-



stant, the mean value of 7336 cal. is obtained for the heat of formation of the solid amalgam, the different values agreeing satisfactorily. The polarisation E. M. F. is very nearly equal for solutions of silver and mercurous nitrates, but is lower for mixtures than for either of the pure solutions.

L. M. J.

**Equilibrium in the System: Water, Ammonium Chloride, Ferric Chloride.** By E. C. J. MOHR (*Zeit. physikal. Chem.*, 1898, 27, 193—221).—During the crystallisation of solutions containing ammonium chloride and ferric chloride, crystals are obtained containing both salts, and Schroeder van der Kolk considered these to be an isomorphous mixture of ammonium chloride with a regular hydrated ferric chloride (Abstr., 1893, ii, 280). This view was, however, contested by Retgers (Abstr., 1894, ii, 85), and the author therefore reinvestigated the equilibrium relations of the systems. Solubility determinations were made at 15°, 25°, 35°, and 45°; four phases may occur, (1) hydrated ferric chloride, (2) Fritsche's double salt,  $\text{FeCl}_3 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ , (3) mixed crystals, (4) ammonium chloride. The ammonium chloride content at the triple point (1·2), and the ferric chloride content at the triple point (2·3), are respectively almost unaffected by temperature, so that the triple-phase curves cut at about -15° probably, where the double salt phase must disappear. The composition of the mixed crystals deposited from various solutions was determined, and although the percentage of iron in the crystals increased with that in the solution, no regular results could be obtained. Microscopic examination of the crystallisation of ferric chloride solutions showed that the regular crystals of Kolk are best formed in an impure atmosphere and are probably due to the presence of ammonia, whilst the quantity formed by the crystallisation of mixtures increases with the quantity of ammonium chloride added; analyses gave results agreeing with  $\text{NH}_4\text{Cl} \cdot 2\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ . The crystals are isotropic, the form being usually a cube with also the faces O and  $\infty\text{O}$ . Another double salt, in the form of olive-brown needles, probably rhombic, was found, possessing the composition  $\text{FeCl}_3 \cdot \text{NH}_4\text{Cl}$ , but it soon changes to the ordinary double salt. The author is unable to draw any definite conclusion regarding the composition of the mixed crystals, but considers them to most probably consist of ammonium chloride containing dissolved Fritsche's double salt.

L. M. J.

**Velocity of Crystallisation. II.** By FRIEDRICH W. KÜSTER (*Zeit. physikal. Chem.*, 1898, 27, 222—226. Compare Abstr., 1898, ii, 330).—The velocity of crystallisation is the velocity with which the surface of a growing crystal extends into the liquid, and is only proportional to the velocity with which the limit of crystallisation extends, when the arrangement of the crystals remains constant. This is the case with moderate undercooling, when Tammann's results show that the velocity is proportional to the undercooling. This does not follow theoretically from Tammann's assumption, and has to be explained by an unknown "influence of the crystals on the liquid," but the author considers no theory valid which does not predict this proportionality. The author

again contests Tammann's supposition that the melting point temperature prevails at the limiting surface; this could only be the case when the convergency temperature (Nernst and Abegg, *Abstr.*, 1895, ii, 155) and melting point are equal (*Abstr.*, 1898, ii, 425).

L. M. J.

**Microscopic Examination of Crystals.** By J. L. C. SCHRÖDER VAN DER KOLK (*Zeit. anal. Chem.*, 1898, 37, 525—580).—This paper is a highly condensed account of the employment of the polarising microscope in the examination and identification of crystalline substances. The greater part of it, dealing with the principles of crystallography and the theory of polarised light, presents no novelty, but many useful practical hints are interspersed amongst well-known matter. Thus, a convenient method of crystallising substances in the cold consists in placing a drop of the solution in the middle of a thin cover-glass, and inverting this over a deep cavity in a glass slide, with a drop of concentrated sulphuric acid at the bottom, so as to form a micro-desiccator, which can be placed on the stage of the microscope. The same apparatus serves for treating substances with the vapours of volatile liquids whilst under observation. For ascertaining the refractive index of a crystal, it is moistened with liquids of different refractive indices, and that liquid is selected which, by suppressing total refraction at the edges of the crystal, renders it invisible. A table of appropriate liquids is given. A valuable means of distinguishing uniaxial from biaxial crystals is afforded by mounting them on the plane face of a glass hemisphere, which is supported by its convex surface in the opening of the microscope stage. It is then possible to give a needle-shaped crystal, which lies in the centre of the field of view, a movement of rotation round its own axis, whilst keeping it both in the centre of the field and in focus. Finally, detailed descriptions are given of the appearance exhibited by about 50 common crystalline substances.

M. J. S.

**A New Asbestos Filtering Tube.** By ADOLF GOSKE (*Chem. Zeit.*, 1898, 22, 21).—The improved filter may be recommended on account of the small amount of asbestos required. Its essential part is a hollow glass ball with two small holes in its upper part, and drawn out at the bottom. The top is covered with a layer of asbestos about 5 mm. thick, and a sufficient quantity of asbestos fibre suspended in water is poured over it. A filter pump is used.

L. DE K.

**Lubricants for Glass Stopcocks.** By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1898, 20, 678—681).—The author points out that a good lubricant for stopcocks should satisfy the following requirements. It should adhere to the glass and not be loosened by water. It should be little affected by changes of temperature. It should not be saponified by alkali, and be sufficiently translucent to render visible any clogging of the hole in the stopcock plug while in use, and to show whether air spaces occur between the plug and the walls of the stopcock.

Two mixtures are recommended: (1) melt 70 parts of pure caout-

chouc and stir in 25 parts of spermaceti and 5 parts of vaselin ; in winter, a little more of the latter should be used ; (2) 70 parts of pure, fresh caoutchouc is melted, and 30 parts of unbleached beeswax is stirred in.

L. DE K.

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## Inorganic Chemistry.

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**Electrolytic Formation of Hydrogen Peroxide.** By FRITZ HABER and S. GRINBERG (*Zeit. anorg. Chem.*, 1898, 18, 37—47).—The authors, on repeating their experiments on the electrolysis of hydrochloric acid (*Abstr.*, 1898, ii, 215 and 365), find that there is no formation of hydrogen peroxide, as previously stated. The test which they employed consisted in shaking the electrolyte with mercury, and then treating with titanous acid. They now find that the small quantity of hydrogen peroxide previously detected is produced by the action of the air and the finely divided mercury during the filtration. Experiments with platinum and gold electrodes show that if hydrogen peroxide is formed, it is destroyed by a secondary reaction, which takes place according to the equation  $\text{H}_2\text{O}_2 + \text{O} = \text{H}_2\text{O} + \text{O}_2$ , and such a small quantity remains undecomposed that it is not possible to detect it. E. C. R.

**Reactions of Metallic Fluorides.** By EMMANUELE PATERNÒ and UGO ALVISI (*Gazzetta*, 1898, 28, ii, 18—24).—Those metallic oxalates which are sparingly soluble or insoluble in water are less soluble in hydrofluoric acid than in solutions acidified with hydrochloric or sulphuric acid.

On adding oxalic acid to a hydrogen fluoride solution of cupric fluoride, cupric oxalate,  $2\text{CuC}_2\text{O}_4 + \text{H}_2\text{O}$ , separates, and only traces of copper remain in solution. Although solutions of manganese chloride, nitrate, or sulphate in the corresponding acid are not precipitated by oxalic acid, yet on adding oxalic acid to a hydrogen fluoride solution of manganese fluoride and warming, a granular, white precipitate of manganous oxalate,  $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is obtained, and only traces of manganese remain in solution. Oxalic acid does not give a precipitate with mercuric chloride solution, but throws down mercuric oxalate from a solution of mercuric fluoride in hydrofluoric acid.

On heating powdered fluorspar with concentrated oxalic acid solution on the water-bath, the fluorine is slowly but wholly eliminated; the same occurs with magnesium fluoride and the fluorides of the cerite earths, yttria, thoria, &c.; this fact may be applied in the analysis of incandescent gas-lamp mantles. Concentrated tartaric acid solution decomposes fluorspar completely on the water-bath, although more slowly than oxalic acid.

Sulphurous anhydride acts on cupric fluoride, depositing Chevreul's salt of the composition  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 + 2\text{H}_2\text{O}$  in minute, red crystals; the precipitation is, however, incomplete. An acid solution of silver fluoride is precipitated by arsenates, chromates, nitrites, platinichlorides, and sulphurous acid. W. J. P.

**Reactions of Fluoro- and Fluoroxysalts.** By EMMANUELE PATERNO and UGO ALVISI (*Gazzetta*, 1898, 28, ii, 24—29).—On treating, with aqueous oxalic acid, solutions of the silicofluoride, fluoroxysulfate, fluoroxymolybdate and the hydrogen fluoride of potassium, potassium quadroxalate separates and the corresponding fluoro- or fluoroxy-acid remains in solution; the silicofluorides of cerium, lanthanum, yttrium, &c., behave similarly, all the fluorine being eliminated from the salt.

On heating cryolite with concentrated oxalic acid solution on the water-bath, hydrogen fluoride is evolved, the aluminium fluoride being first decomposed and subsequently the sodium fluoride; similarly, on passing steam over red-hot cryolite, alumina, hydrogen fluoride, and sodium fluoride are first formed, and in a second stage of the reaction the sodium fluoride is attacked by the water vapour. Triplite is also decomposed by heating with oxalic acid solution.

Tartaric acid in aqueous solution also decomposes potassium silicofluoride and cryolite.

W. J. P.

**Ozone.** By ALBERT LADENBURG (*Ber.*, 1898, 31, 2508—2513).—Ozonised oxygen is condensed by means of liquid air and then allowed to partially evaporate, by which the residue is rendered much richer in the less readily volatile ozone. This operation is again repeated and the ozone finally allowed to evaporate; in this way, a gas is obtained which contains 86.16 per cent. by weight of ozone, and has a density of 1.3698 as compared with oxygen, the density being calculated from the rate of effusion determined in Schilling's apparatus. From these data, it follows that the density of pure ozone would be 1.456 as compared with oxygen, whereas the theoretical density is 1.5.

Ozone is not so soluble in water as is usually supposed, since at the normal pressure and ordinary temperature, water only absorbs 0.01 volume or 0.00002 part by weight.

An attempt was made to determine the boiling point of ozone by condensing ozonised oxygen, allowing the oxygen to evaporate, and then ascertaining the temperature at which the residual ozone evaporated. The oxygen volatilised at  $-186^{\circ}$  leaving 4—5 c.c. of an almost black opaque liquid. The temperature as indicated by the thermometer then rose to  $-125^{\circ}$ , at which point the apparatus exploded violently, so that this can only be taken as a lower limit.

A. H.

**Ogier's Sulphur Oxychloride.** By RUDOLPH JOH. KNOLL (*Ber.*, 1898, 31, 2183—2185).—This alleged compound,  $S_2OCl_4$  (*Abstr.*, 1882, 694), is in reality a mixture of sulphur dichloride, thionyl chloride, and sulphuryl chloride, approximately in the proportions,  $17S_2Cl_2 + 2SOCl_2 + 5_2SOCl_2$ . When it is distilled alone (under 50 mm. pressure), the first fraction of the distillate has not quite the same composition as the last. When it is distilled with sulphur, thionyl and sulphuryl chlorides distil over, and finally sulphur chloride,  $S_2Cl_2$ , which must have been formed by the action of the sulphur on the sulphur dichloride present.

C. F. B.

**Atomic Weight and Derivatives of Selenium.** By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1898, 20, 555—579).—Two series of determinations of the atomic weight of selenium were made by analys-

ing carefully purified silver selenite,  $\text{Ag}_2\text{SeO}_3$ , and ammonium selenibromide,  $(\text{NH}_4)_2\text{SeBr}_6$ . The silver employed in preparing the former was purified by Stas's method and converted into nitrate; the selenious anhydride was prepared from pure selenium by means of nitric acid, and was purified by repeated sublimation. On dissolving it in water and adding the purified silver nitrate, a white precipitate of silver selenite was obtained which crystallised from dilute nitric acid in anhydrous plates having a sp. gr. = 5.9297. The analyses were carried out by expelling the selenium completely in the form of dioxide, by passing hydrogen chloride over the salt contained in a porcelain boat, heated in a combustion tube; the residue of silver chloride was weighed, and was then reduced by purified hydrogen to metallic silver, and the latter weighed. The average of eleven experiments gives as the atomic weight of selenium, calculated from the silver chloride formed, the value 79.329 ( $O = 16$ ), the probable error being  $\pm 0.009$ ; exactly the same value was obtained from the weight of reduced silver in eight of these experiments. Attempts to obtain sodium selenite sufficiently pure to serve as a means of determining the atomic weight of selenium failed. Ammonium selenibromide, however, was readily prepared pure by dissolving ammonium bromide (9 parts) in water, adding selenium (4 parts) and a slight excess of bromine until a clear solution was obtained, and heating on the water-bath until the excess of bromine was expelled; on slow evaporation, crystals of ammonium selenibromide separated, which were purified by repeated crystallisation. Special care was taken to purify the materials used in preparing the salt. The latter was analysed by precipitating the selenium by hydroxylamine hydrochloride, according to Keller's method (Abstr., 1898, ii, 575), and the mean of eight experiments gave a value 79.285 ( $O = 16$ ) for the atomic weight, with a probable error  $\pm 0.011$ . The general mean of all the author's experiments is 79.314.

*Double Bromides of Selenium.*—Although potassium and ammonium selenibromides are easily obtained by adding potassium or ammonium bromide to an aqueous solution of selenium tetrabromide (Muthmann and Schäfer, Abstr., 1893, ii, 318), the corresponding sodium and lithium salts do not appear to exist. The selenibromides of *rubidium*,  $\text{Rb}_2\text{SeBr}_6$ , and *cæsium*,  $\text{Cs}_2\text{SeBr}_6$ , are somewhat less soluble than the corresponding potassium salt, although closely resembling it in crystalline form; they are best prepared by adding a slight excess of bromine to a solution of the alkali bromide containing in suspension the theoretical amount of selenium, and evaporating on the water-bath until crystals separate. Corresponding organic salts containing selenium can be prepared by adding the hydrobromide of a base, dissolved in alcohol, to an alcoholic solution of selenium dioxide in concentrated hydrobromic acid. They are all decomposed by water, and prolonged digestion with ether extracts selenium tetrabromide. *Methylamine selenibromide*,  $(\text{NH}_2\text{Me})_2\text{H}_2\text{SeBr}_6$ , separates from alcohol containing hydrobromic acid in well defined red crystals; *ethylamine selenibromide*,  $(\text{NH}_2\text{Et})_2\text{H}_2\text{SeBr}_6$ , forms red, hexagonal prisms. The *dimethylamine* salt,  $(\text{NHMe}_2)_2\text{H}_2\text{SeBr}_6$ , and the *trimethylamine* salt,  $(\text{NMe}_3)_2\text{H}_2\text{SeBr}_6$ , separate from alcohol in red crystals, whilst *tetretethylammonium selenibromide*,  $(\text{NEt}_4)_2\text{SeBr}_6$ , forms

flat, hexagonal plates. On adding the hydrobromides of aniline and diphenylamine to an aqueous solution of selenium tetrabromide, no double salt is formed, but the selenium is almost completely precipitated in the free state. Phenylhydrazine and quinoline act similarly; pyridine hydrobromide, however, gives rise to the salt,  $(C_5H_5N)_2, H_2SeBr_6$ , which crystallises from alcohol in deep-red leaflets or prisms, but is decomposed by other solvents. The *piperidine* salt,  $(C_5H_{11}N)_2, H_2SeBr_6$ , which crystallises from alcohol in red plates, closely resembles the pyridine derivative.

*Existence of Selenium Monoxide* (compare Pierce, Abstr., 1898, ii, 403).—In subliming large quantities of pure selenious anhydride, no odour similar to that attributed by Berzelius to selenium monoxide was noticeable. On heating a mixture of equivalent quantities of selenium and its dioxide, either in an open vessel, or in a sealed tube, to the boiling temperature of selenium, no interaction took place, and no gaseous product could be detected. Selenium monobromide does not act on dry silver oxide below  $20^\circ$ , but at this temperature a violent action takes place, selenious anhydride alone being formed. From these experiments, it is concluded that selenium monoxide does not exist (compare Chabrie, *Ann. Chim. Phys.*, 1890, [vi], 20, 273).

W. A. D.

NOTE BY ABTRACTOR.—Norris (Abstr., 1898, i, 510), has already described the salt,  $(NHMe_2)_2, H_2SeBr_6$ , prepared from dimethylamine, and in addition has obtained the salts,  $3NHMe_2, HBr, SeBr, 2SeBr_4$ ;  $2(NHMe_2, HBr)_2, SeBr_4$ ;  $2(NHMe_2, HBr)_2, SeBr_4$ ; and  $2(NHMe_2, HBr)_2, NHMe_2, HBr, SeBr_4$ .

Similar salts were also obtained from trimethylamine.

**Copper Selenate. Preparation of Selenic Acid.** By RENÉ METZNER (*Compt. rend.*, 1898, 127, 54—57).—A solution of selenious acid was oxidised by a current of chlorine, the reaction being accompanied by the development of 30 Cal., and the solution of selenic acid thus obtained was neutralised with pure cupric oxide. On cooling the liquid, after concentration by evaporation, pale blue prisms of copper selenate,  $CuSeO_4 + 5H_2O$ , were deposited. Attempts were made to substitute bromine for chlorine in the preparation of the salt, but it was found that the oxidation of the selenious acid was never complete. The solubility of copper selenate varies greatly with the temperature; 1 litre of the saturated solution was found to contain 257 grams of the salt at  $15^\circ$ , 346 grams at  $35^\circ$ , and 435 grams at  $55^\circ$ . At about  $70^\circ$ , the solution undergoes decomposition, with formation of a green, crystalline deposit which is seen under the microscope to consist of small, monoclinic prisms. This compound was first obtained, but not analysed, by Mitscherlich; the author's analyses show that it has the composition  $2CuSeO_4, CuO + 5H_2O$ . When crystallised from a solution containing a large excess of selenic acid, copper selenate forms microscopic, transparent, tabular crystals of the composition  $CuSeO_4 + 2H_2O$ . The crystals lose water on exposure to a dry atmosphere, and when dried at  $100^\circ$  only one molecule of water is retained. The heat of formation of copper selenate (18.12 Cal.) was deduced from the heat developed (13.06 Cal.) on precipitating a

normal solution of the salt with the equivalent amount of potash. The heat of dissolution is  $-2.66$  Cal.

Selenic acid was obtained in a very pure state by the electrolysis of a saturated solution of copper selenate with a current of 5 ampères at 2—3 volts. N. L.

**Decomposition of Nitric Acid by Heat at Moderate Temperatures.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 127, 83—88).—Small quantities of pure nitric acid were introduced into tubes previously made vacuous and having a volume about 20 times that of the liquid, and the tubes were then kept in the dark at the ordinary temperature for several weeks; the nitric acid remained unaltered. When, however, similar tubes are heated at  $100^{\circ}$ , also in the dark, the nitric acid decomposes into nitric peroxide, oxygen, and water, and the decomposition at first increases with the time, but the rate of increase gradually falls. The decomposition is always incomplete and is limited chiefly by the water produced. Nitric acid of sp. gr. 1.333 undergoes practically no change at  $100^{\circ}$  under similar conditions.

The decomposition can scarcely be regarded as reversible, since the oxygen will combine very slowly with any nitrous acid that may be formed by the action of the nitric peroxide on the water. The decomposition of nitric acid into nitric peroxide, oxygen, and water at  $100^{\circ}$  would absorb about  $-6.5$  Cal. per molecule of acid. The decomposition of nitric anhydride absorbs much less, hence the instability of this compound. On the other hand, the heat of formation of hydrated nitric acid is much higher than that of the anhydrous acid, hence the greater stability of the former. C. H. B.

**Action of Free Hydrogen on Nitric Acid.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 127, 27—29).—Sealed tubes containing known quantities of hydrogen and concentrated nitric acid were exposed to direct sunlight for two weeks, kept in the dark during the same period, and heated at  $100^{\circ}$  for 1 to 5 hours. In every case, the original volume of hydrogen employed was recovered on examining the contents of the tubes, even when the experimental conditions had been such that the nitric acid itself was decomposed, with liberation of oxygen. This inactivity of hydrogen towards nitric acid is in striking contrast with its behaviour with concentrated sulphuric acid, which is acted on at the ordinary temperature with formation of sulphurous acid.

The liberation of oxygen from pure nitric acid takes place at  $100^{\circ}$  and also, under the influence of light, in the cold; it does not take place in the dark at the ordinary temperature. The author's observations on this point will be published hereafter. N. L.

**Action of Dilute Nitric, Sulphuric, Hydrochloric and Phosphoric Acids on Nitrates in the Presence of Ether.** By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 497—503).—It has previously (Abstr., 1897, ii, 255) been shown that the presence of nitrates raises the coefficient partition of dilute nitric acid between ether and water. This property affords a basis for a method of extracting free nitric acid from solutions of nitrates by the aid of ether.



The reaction between dilute sulphuric acid and an excess of potassium nitrate is represented as follows:  $\text{H}_2\text{SO}_4 + 2\text{KNO}_3 = \text{HNO}_3 + \text{KNO}_3 + \text{KHSO}_4$ . If the nitric acid thus formed is removed by ether, then the acid sulphate tends to dissociate under the influence of the water into sulphuric acid and the normal sulphate. The sulphuric acid will then act on a further amount of potassium nitrate according to the above equation, until the whole of the sulphuric acid has been converted into normal sulphate, as if the reaction had taken place according to the equation  $\text{H}_2\text{SO}_4 + 2\text{KNO}_3 = \text{K}_2\text{SO}_4 + 2\text{HNO}_3$ . This has been proved experimentally by taking 20 c.c. of water containing 0.20 gram of sulphuric acid, dissolving in this 5 grams of potassium nitrate, and extracting with 200 c.c. of ether, the extraction being repeated six times.

Hydrochloric acid reacts in the same manner as sulphuric acid. Phosphoric acid reacts according to the equation  $\text{H}_3\text{PO}_4 + \text{KNO}_3 = \text{HNO}_3 + \text{KH}_2\text{PO}_4$ .

Nitric acid acting on normal sulphates gives acid sulphates; the acid sulphate does not sensibly dissociate, yielding free sulphuric acid. The action between nitric acid and chlorides is not appreciable.

J. J. S.

**Homogeneity of Helium.** By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1898, 52, 316—324).—The gas was separated into six fractions by diffusion through a piece of pipe stem. Fraction No. 1 was then pumped into the diffusion vessel, one half of it was diffused and transferred to vessel No. 1; fraction No. 2 was then added, and one-third of the mixture diffused and transferred to vessel No. 1; fraction No. 3 was then added, and one half of the whole diffused and transferred to vessel No. 2; fraction No. 4 added and one half diffused and transferred to vessel No. 3, and so on. After four such complete fractionations in the case of air, the extreme fractions contained 17.37 and 22.03 per cent. of oxygen respectively. In the case of nitrogen, prepared from solutions of ammonium chloride and sodium nitrite, with some copper sulphate, thirty fractionations produced no alteration in density. Repeated fractionations of samples of helium from samarskite and cleveite resulted in the separation of helium with density 1.98 and refractivity 0.1238 as the lightest fraction, and a very little nearly pure argon as the heaviest fraction. The light fraction was apparently pure helium, as further diffusion did not alter its density. "It appears, therefore, that helium contains no unknown gas, nor is it possible to separate it by diffusion into any two kinds of gas; all that can be said is that most minerals which evolve helium also evolve argon in small quantity."

The authors had hoped to find an element with density = 10 and atomic weight = 20; they still regard the existence of such an element as probable, for it would form with  $\text{He} = 4$  and  $\text{A} = 40$  a triad like  $\text{F} = 19$ ,  $\text{Cl} = 35.5$ ,  $\text{Mn} = 55$  and many similar triads occurring in the groups of the periodic table.

C. F. B.

**Conversion of Potassium Iodide and Bromide into Potassium Chloride.** By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1898, 18, 77—82).—Potassium iodide is easily and completely con-

verted into potassium chloride by heating it in a porcelain crucible in a current of chlorine. Potassium bromide, on the other hand, cannot be completely converted into chloride by means of a current of dry chlorine unless it is heated to such a high temperature that potassium chloride begins to volatilise. In the presence of water, however, the conversion into chloride is complete at moderate temperatures. The potassium bromide (2.49 grams) is treated in a small Erlenmeyer flask with 1 c.c. of water and a drop of hydrochloric acid and then heated in a brisk current of chlorine. The flask is placed on an asbestos plate with another asbestos plate 2 c.c. below the first and under this a small burner. After 1—1½ hours heating below the boiling point, the water is evaporated off and finally the asbestos plate on which the flask rests is heated to redness for a short time, and the operation repeated until a constant weight is obtained. E. C. R.

**Specific Gravity of Sodium Chloride Solutions.** By H. C. HAHN (*J. Amer. Chem. Soc.*, 1898, 20, 621—630).—This is an elaborate investigation as to the best way of accurately determining the sp. gr. of sodium chloride solutions. To be of any real value, the sp. gr. at 15.08° should be exact to the fourth place of decimals. In this case, if  $S$  = the sp. gr., the percentage of sodium chloride will be  $60,209,585 - 626,853,1S + 1067,352,667S^2 - 633,92S^3 + 133,333,333S^4$ . A main factor in determining the sp. gr. is the knowledge of the sp. gr. of the air in the balance case, which depends on the pressure, temperature, moisture, and the amount of carbonic anhydride. For further particulars, the original paper should be consulted, the results being set forth in a very comprehensive table. L. DE K.

**Action of Sodium Metarsenite on Metallic Salts.** By C. REICHARD (*Ber.*, 1898, 31, 2163—2171).—When sodium metarsenite,  $\text{Na}_2\text{As}_2\text{O}_4$ , was added to excess of a solution of a metallic salt, free

Composition.	Metallic salt used.	Properties.
$\text{Ni}_3\text{As}_2\text{O}_6$ $\text{Pb}_3\text{As}_2\text{O}_6$ $\text{Zn}_3\text{As}_2\text{O}_6$ $\text{Sn}_3\text{As}_2\text{O}_6$	$\text{Ni}(\text{NO}_3)_2$ $\text{Pb}(\text{NO}_3)_2$ $\text{ZnSO}_4$ $\text{SnCl}_2$	Bright green, amorphous powder. Heavy, white powder. Crystallises from ammonia in white needles. Yellowish-white; decomposed by acids and alkalis with separation of metallic arsenic.
$\text{Co}_2\text{As}_2\text{O}_5$ $\text{Cd}_2\text{As}_2\text{O}_5$	$\text{Co}(\text{NO}_3)_2$ $\text{CdSO}_4$	Amethyst-coloured mass. White substance.
$\text{Cu}_4\text{As}_2\text{O}_7$ $\text{Fe}_4\text{As}_2\text{O}_9$ $\text{Mn}_5\text{As}_2\text{O}_8$ $\text{Hg}_5\text{As}_2\text{O}_8$	$\text{CuSO}_4$ $\text{FeSO}_4$ $\text{MnSO}_4$ $\text{HgCl}_2$	Green, amorphous powder. Greenish-white substance, turning rusty in the air. White, turning pink to brown in the air. White mass, turning yellow and decomposing in daylight.
$\text{Sn}_7\text{As}_2\text{O}_{17}$ $\text{Ag}_6\text{As}_4\text{O}_9$	$\text{SnCl}_4$ $\text{AgNO}_3$	Yellowish-white mass. Yellowish substance, decomposed by caustic soda with separation of metallic silver.

acid was always liberated, and the precipitate was in 4 cases (enumerated first in the table) an orthoarsenite, in 2 (the next two) a pyroarsenite, but in no case was it a metarsenite. The substances prepared are described in the table (p. 23). C. F. B.

**Action of Hydrogen on Silver Sulphide.** By H. PÉLABON (*Compt. rend.*, 1898, 126, 1864—1866).—Hydrogen acts on silver sulphide in sealed tubes above  $250^{\circ}$ , the proportion of hydrogen sulphide formed at first increasing with the time but eventually becoming constant. Conversely, in a tube containing silver and hydrogen sulphide, the quantity of the latter gradually diminishes until it reaches a limit. At any given temperature above  $350^{\circ}$ , the limit is the same, whether the initial system contained hydrogen sulphide and silver, or silver sulphide and hydrogen. The ratio,  $\rho$ , of the partial pressure of the hydrogen sulphide to the total pressure of the mixture diminishes as the temperature rises and the curve that represents it as a function of the temperature approaches the axis of the abscissæ as the temperature increases. Between  $360^{\circ}$  and  $700^{\circ}$ , the curve is identical with a straight line passing through the points  $\rho = 0.21$ ,  $t = 360^{\circ}$ , and  $\rho = 0.16$ ,  $t = 700^{\circ}$ . Whatever the initial system, equilibrium is reached more quickly the higher the temperature; at  $360^{\circ}$ , about 160 hours is necessary, whilst at  $580^{\circ}$  a few moments suffice. At a given temperature, the limit value of  $\rho$  is independent of the physical condition of the silver or silver sulphide, and, moreover, is the same if the initial system consisted of silver, hydrogen, and sulphur. The silver liberated from the silver sulphide forms filiform masses only when the temperature is below  $580^{\circ}$ , and the best specimens are obtained by heating crystallised silver sulphide and hydrogen in sealed tubes at  $440^{\circ}$ . C. H. B.

**Heat of Formation of Lithium Carbide.** By ANTOINE GUNTZ (*Compt. rend.*, 1898, 126, 1866—1868).—The action of water on lithium carbide,  $C_2Li_2$ , develops +37.10 Cal., and hence  $C_2$  (diamond) +  $Li_2$  sol. =  $C_2Li_2$  (sol.) develops +11.3 Cal., a value which is much higher than the corresponding values for sodium or calcium, and explains the formation of lithium carbide under such varied conditions. When the carbide is prepared by the direct action of lithium on carbon, the mixture must be placed in an iron dish in a hard glass tube enclosed in a glazed porcelain tube, and the tubes must be made vacuous, because lithium readily combines with nitrogen. The temperature must not exceed a dull red heat, otherwise the carbide dissociates. Even the diamond is attacked by lithium at this temperature. The carbide cannot be obtained by heating carbon with lithium carbonate, because the latter volatilises before it dissociates.

When the carbide is added to fused lithium chloride, lithium subchloride and carbon are formed, but at a high temperature the subchloride dissociates into the normal chloride and lithium, and the latter attacks the carbon, and these changes go on until a condition of equilibrium is established. These observations explain why a carbon cathode cannot be used for the isolation of lithium by electrolysis of the fused chloride. C. H. B.

**Calcium Hydride.** By HENRI MOISSAN (*Compt. rend.*, 1898, 127, 29—34).—Calcium hydride is obtained by heating crystallised calcium (Abstr., 1898, ii, 578), contained in a nickel boat, to dull redness in an atmosphere of dry hydrogen. Comparison of the weight of metal employed with the weight of hydride obtained, and measurement of the volume of hydrogen evolved on treating the substance with water, show that the hydride has the composition  $\text{CaH}_2$ . Obtained as above, calcium hydride forms a white, fused mass of crystalline fracture, which is shown by microscopic examination to consist of slender, transparent plates; it has a sp. gr. = 1.7. When heated to  $600^\circ$  in a vacuum, no appreciable dissociation occurs; nor is the hydride affected by heating in hydrogen at the melting point of glass. It is decomposed by the halogens at a dull red heat, with incandescence. When heated to redness in air or oxygen, it burns brilliantly, and sufficient heat is evolved to cause fusion and crystallisation of the calcium oxide formed. Calcium hydride is decomposed by heating in sulphur or phosphorus vapour, but no action was observed with selenium at the melting point of glass, or with nitrogen, silicon, and boron. When heated at  $700\text{--}800^\circ$  with finely-divided carbon, calcium hydride is partially decomposed, with production of calcium carbide. Metallic fluorides, sodium chloride, and silver iodide are decomposed when heated with calcium hydride, but potassium iodide is not acted on. Chlorates, perchlorates, bromates, or permanganates, and similar oxidising agents, are reduced with explosive violence. Hydrogen sulphide, nitric oxide, and carbonic anhydride are also decomposed at a red heat. Calcium hydride is readily decomposed by water and by dilute acids; concentrated sulphuric and nitric acids, however, have but little action in the cold. Benzene, turpentine, and alkyl chlorides and iodides, when free from water, are without action on calcium hydride; ethylic alcohol slowly attacks it. The vapour of carbon tetrachloride is decomposed, with incandescence, at about  $400^\circ$ .

N. L.

**Solubility of Lime in Water at Different Temperatures.** By ALEXANDER HERZFELD (*Bied. Centr.*, 1898, 27, 571; from *Oesterr. Zeits. Zuckerind.*, 1897, 1197).—The amounts of water required to dissolve 1 part of  $\text{CaO}$  at different temperatures are as follows.

15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°
776	813	848	885	924	962	1004	1044	1108	1158	1244	1330	1410	1482

N. H. J. M.

**Solubility of Lime in Aqueous Solutions of Sodium and Potassium Chloride.** By GODFREY L. CABOT (*J. Soc. Chem. Ind.*, 1897, 16, 417—419).—Curves are given which show that the solubility of lime in solutions of either sodium or potassium chloride is a maximum for all temperatures when the solution contains about 60 grams of the salt per litre; it is a minimum at any fixed temperature when the solution is saturated, the solubility then being much less than in pure water of the same temperature. A solution of sodium chloride dissolves more lime at all temperatures and concentrations than a corresponding solution of potassium chloride. In

all cases, the maximum solubility of lime in the chloride solution occurs when the temperature is lowest; with solutions of all concentrations, the solubility decreases regularly as the temperature increases.

W. A. D.

**Formation and Composition of Bleaching Powder.** By HUGO DIRTZ (*Chem. Zeit.*, 1898, 22, 7—9).—The author regards the formation of bleaching powder as taking place in several stages. The first action of chlorine on the slaked lime is to give  $(\text{CaO}, \text{CaCl} \cdot \text{OCl} + 2\text{H}_2\text{O})$ ; further action gives  $(2\text{CaCl} \cdot \text{OCl} + \text{CaO}, \text{CaCl} \cdot \text{OCl} + 4\text{H}_2\text{O})$ ; yet further action,  $(6\text{CaCl} \cdot \text{OCl} + \text{CaO}, \text{CaCl} \cdot \text{OCl} + 8\text{H}_2\text{O})$ . In practice, the reaction seems to stop here; theoretically, it might continue indefinitely, yielding successive members of the series  $[(2n-2)\text{CaCl} \cdot \text{OCl} + \text{CaO}, \text{CaCl} \cdot \text{OCl} + 2n\text{H}_2\text{O}]$ . Most bleaching powders consist of mixtures of the first three members, ( $n=0, 1, 2$ ), the formulæ of which are given above; but of the numerous published analyses of bleaching powders, some are found to correspond very well with these three; three such analyses are quoted below.

	$n=0.$		$n=1.$		$n=2.$	
	Found.	Calc.	Found.	Calc.	Found.	Calc.
Total CaO .....	52.12	51.14	44.12	44.01	41.27	41.14
Available Cl .....	31.44	32.42	41.05	41.85	44.5	45.64
CaO from CaO, CaCl·OCl...	27.33	25.57	11.80	11.00	5.40	5.14

It is shown that these views allow of a satisfactory explanation of the reactions of bleaching powder with carbonic anhydride, with sulphurous anhydride, and with acetic acid, and of its behaviour when heated. It is proposed to perform experiments with a view to testing their truth further.

C. F. B.

**Decomposition of Barium and Calcium Dihydrogen Phosphates by Water at 100°.** By GEORGES VIARD (*Compt. rend.*, 1898, 127, 178—180).—The monobasic phosphates of the alkaline earths are known to undergo partial decomposition by water at the ordinary temperature, with liberation of phosphoric acid and precipitation of a dibasic phosphate. The author has studied the decomposition of monobarium and monocalcium phosphates by water at 100°, and finds the reaction to be similar to that which occurs in the cold, the quantitative results, however, are different. As the weight of monobasic phosphate which is heated with a constant weight of water increases, the ratio of the total phosphoric acid remaining in solution to the combined phosphoric acid also increases, at first rapidly and then more slowly, until it becomes sensibly constant. The limiting value of this ratio was found to be 2.8 for the barium, and 2.34 for the calcium, salt; in the cold, the values obtained by Joly were 2.0 and 1.5 respectively. Analysis shows that the precipitate consists only of the dibasic phosphate, unless a saturated solution has been employed, in which case the precipitate is contaminated with undissolved monobasic phosphate. It is to be observed that the precipitated dicalcium phosphate is always anhydrous and insoluble in acetic acid, whereas,

if the decomposition takes place in the cold, the hydrated phosphate,  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 + 4\text{H}_2\text{O}$ , is formed, which is soluble in acetic acid.

The composition of the precipitate being once determined, the ratio  $R$ , of the total to the combined phosphoric acid may be calculated from the weight of the precipitate. For, if  $P$  is the weight of monobasic phosphate employed,  $M$  its molecular weight,  $p$  the weight of dibasic phosphate precipitated,  $m$  its molecular weight, and  $q$  the molecular weight of phosphoric anhydride, then the weights of the latter contained in  $P$  and  $p$  are  $Pq/M$  and  $pq/m$  respectively and

$$R = \left( \frac{P}{M} - \frac{p}{m} \right) \div \left( \frac{P}{M} - 2\frac{p}{m} \right) \quad \text{N. L.}$$

**Anhydrous Crystalline Magnesium Sulphide.** By A. MOURELOT (*Compt. rend.*, 1898, 127, 180—183).—Amorphous magnesium sulphide is best prepared by passing a current of hydrogen sulphide over a mixture of sulphur with magnesium filings contained in a carbon boat, which is placed in a porcelain tube heated in a reverberatory furnace. The sulphide is thus obtained as a white, or slightly grey, mass, which analysis shows to have the composition  $\text{MgS}$ . Another method of preparation consists in passing hydrogen sulphide over anhydrous magnesium sulphate or oxide heated to about  $1200^\circ$ ; in this, however, the action is much slower.

When the amorphous sulphide is heated for a few minutes in the electric furnace, it is converted into a globular mass of crystalline fracture, which is shown by analysis to have the same composition as the amorphous sulphide; the crystalline sulphide may be also prepared by heating, in the electric furnace, a mixture of magnesium chloride with stannous sulphide in molecular proportion. Attempts to prepare it by the reduction of magnesium sulphate with carbon gave unsatisfactory results.

The crystalline magnesium sulphide obtained by the methods described above consists of a mass of cubical crystals of sp. gr. = 1.85, which have no action on polarised light, and exhibit two cleavage planes at right angles to each other. It is not acted on by hydrogen at the highest temperature of a reverberatory furnace, but is decomposed, with incandescence, by chlorine at about  $300^\circ$ , with the formation of the chlorides of magnesium and sulphur; bromine and iodine also decompose it at a dull red heat. The crystalline sulphide is readily oxidised when heated in oxygen, and also by heating with potassium chlorate, potassium nitrate, lead peroxide, and phosphoric anhydride. It is not reduced by heating at a high temperature with phosphorus, boron, silicon, or iron; sodium, however, decomposes it. It is readily acted on by steam, with formation of magnesium oxide and hydrogen sulphide; at the ordinary temperature, however, water acts with great difficulty on the crystalline sulphide, whereas the amorphous sulphide is immediately decomposed. Nitric and sulphuric acids and gaseous hydrogen fluoride and chloride act on the crystalline sulphide at the ordinary temperature, whilst hydrogen bromide and iodide react at a dull red heat. It is also readily attacked by phosphorus trichloride and by chromyl chloride; in the

latter case, a greenish substance is produced, the nature of which is being investigated ; it contains both chromium and sulphur.

N. L.

#### Formation of Metallic Sulphides by Mechanical Influences.

By LÉON FRANCK (*Bull. Soc. Chim.*, 1897, [iii], 17, 504—506).—Spring has shown that sulphides of magnesium, zinc, iron, copper, &c., may be obtained by subjecting intimate mixtures of the metals and sulphur to a pressure of 6500 atmospheres (Abstr., 1883, 904 ; 1884, 959), and it has long been known that mercuric sulphide may be obtained by triturating the metal with sulphur, cuprous sulphide by triturating the metal with sulphur under water, and ferrous sulphide in a similar manner with hot water. The author finds that when a mixture of flowers of sulphur and of magnesium powder is rubbed between two sheets of paper, hydrogen sulphide is evolved. A similar reaction occurs with aluminium powder and sulphur, or even when sheet aluminium is rubbed with flowers of sulphur. J. J. S.

**Yttrium Earths in Monazite Sands.** By G. URBAIN (*Compt. rend.*, 1898, 127, 107—108).—Further investigations have confirmed the utility of the method of fractionating by means of ethyl-sulphates ; it is especially valuable for resolving a complex mixture into groups to which the other methods of fractionation can be applied much more easily than to the original substance. The constituents of crude yttria do not separate with uniform distinctness ; it is easy, for example, to obtain erbium quite free from holmium, but very difficult to eliminate erbium from the fractions rich in holmium. By combining the ethyl-sulphate method with some of the older methods, the author finds that the crude yttria from monazite sands consists chiefly of yttrium of atomic weight 89, and contains terbium with an atomic weight as high as 151.4, but no element with the atomic weight 100 or 97. C. H. B.

**Metallic Phosphates.** By ROBERT M. CAVEN and ALFRED HILL (*J. Soc. Chem. Ind.*, 1897, 16, 29—30. Compare Abstr., 1898, ii, 591).—On adding disodium hydrogen phosphate to an aqueous solution of aluminium sulphate, no precipitate is formed at first, but on boiling for an hour, the greater part of the aluminium is precipitated as phosphate. An excess of ammonium chloride partially precipitates aluminium phosphate from a solution of the latter in aqueous ammonia or caustic alkalis. Cold, dilute acetic acid dissolves aluminium phosphate, but, on boiling, the latter is precipitated ; ammonium acetate does not produce a precipitate with the cold solution, nor with a solution of the phosphate in hydrochloric acid to which an excess of acetic acid has been added ; if, however, only a small quantity of acetic acid is present in the latter case, ammonium acetate gives rise to a precipitate of aluminium phosphate. On adding dilute acetic acid and ammonium acetate to a nearly saturated solution of aluminium phosphate in aqueous aluminium sulphate, a precipitate is produced, although none is formed when only a small amount of the phosphate is present ; in the latter case, the addition of a little disodium hydrogen phosphate brings about precipitation.

Chromium phosphate is gradually precipitated on boiling a solution

containing disodium hydrogen phosphate and chromium sulphate; it is not as easily soluble in aqueous ammonia as aluminium sulphate, but resembles the latter in being precipitated by ammonium chloride from its solution in caustic potash. Chromium phosphate is readily soluble in acetic acid, but is precipitated from neutral solutions by ammonium acetate; like ferric phosphate, it undergoes hydrolysis when washed with water.

Traces of chromium and aluminium may be detected in presence of large quantities of ferric phosphate by fusing the mixed phosphates with potassium hydroxide on platinum foil; on adding ammonium chloride to the aqueous extract, aluminium is precipitated as mixed phosphate and hydroxide, and, on filtering, a yellow solution is obtained if chromium is present, becoming green when sulphurous acid is added.

Cupric phosphate is somewhat soluble in aqueous cupric chloride and cupric sulphate, and undergoes hydrolysis when washed with water; on boiling with water, it is converted into a basic phosphate,  $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{CuO} \cdot \text{H}_2\text{O}$ , as stated by Steinscheider (*Abstr.*, 1891, 1423), whilst aqueous potash completely hydrolyses it to cupric oxide.

Bismuth phosphate is somewhat soluble in aqueous bismuth chloride, but is not hydrolysed by boiling water, although completely converted into oxide when boiled with caustic alkalis.

Lead phosphate is insoluble in aqueous lead nitrate, and is not changed when boiled with water; it easily dissolves in boiling caustic potash, but less readily in aqueous ammonia.

W. A. D.

**Influence of Silicon on the Heat of Solution of Coke Cast Irons.** By EDWARD D. CAMPBELL and WILLIAM E. HARTMAN (*J. Amer. Chem. Soc.* 1898, 20, 690—695).—The object of this research was to determine if any thermochemical evidence could be obtained of a change in the condition in which silicon exists in cast iron, this change being due to differences of the temperature at which the iron is made. The solvent was a solution of ammonium copper chloride in the molecular ratio  $(\text{NH}_4\text{Cl})_2\text{CuCl}_2 : 50\text{H}_2\text{O}$ , but with the addition of 0.84 per cent. of free hydrochloric acid. When either from a sufficiently high temperature of the blast furnace at the time the iron is made, or from the presence of a moderate amount of silicon, probably about one and four-tenths per cent., the carbon is nearly all in the graphitic or “graphitic temper” form; then the heat evolved by the oxidation of the silicon, is proportional to the amount of silicon present. When from a low temperature in the furnace accompanied by low silicon, the carbon is largely in the combined form, then the heat rendered sensible is very much diminished owing to the large amount of heat necessary to decompose the compounds of iron and carbon, or possibly compounds of iron, silicon, and carbon, or of carbon and silicon. As the oxidation of one gram of silicon alone develops 3824 Cal., and the results obtained by dissolving cast irons give a maximum of 3303 Cal., it is evident that the compound of silicon with iron must have a very considerable heat of formation. When the percentage of silicon is nearly sufficient to correspond with the empirical formula  $\text{SiFe}_3$ , the compound is insoluble in ammonium copper chloride.

H. C.



**Constitution and Genesis of Iron Sulphates.** By RUDOLF SCHARIZER (*Zeit. Kryst. Min.*, 1898, 30, 209—231).—In an investigation dealing with the genesis of native iron sulphates, the author has made experiments requiring several years for their completion. In this first paper are given the results of experiments on the loss of water, and oxidation of ferrous sulphate.

Over sulphuric acid, ferrous sulphate ( $\text{FeSO}_4 + 7\text{H}_2\text{O}$ ) readily loses three molecules of water,  $3\text{H}_2\text{O}$  more are given off, with partial oxidation of the ferrous sulphate, at  $60-80^\circ$ ,  $\frac{1}{2}\text{H}_2\text{O}$  is lost at  $100-300^\circ$ , whilst the remainder is only given off on ignition. When exposed to air, it effloresces after a long period of time to the end product  $\text{FeSO}_4 + \text{H}_2\text{O}$ . The products of oxidation of a ferrous sulphate solution depend on the lapse of time and on the degree of dilution of the solution; ferric sulphate is also formed [ $10\text{FeSO}_4 + 5\text{O} = \text{Fe}_2\text{SO}_9 + 3\text{Fe}_2(\text{SO}_4)_3$ ], and this by its decomposition [ $3\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O} = \text{Fe}_6\text{SO}_{12} + 8\text{H}_2\text{SO}_4$ ] introduces further complications. One gram of ferrous sulphate in 50 c.c. of water gives a permanent ferric sulphate solution; in more concentrated solutions, soluble basic salts are formed, whilst in more dilute solutions there is free sulphuric acid.

L. J. S.

**Decomposition of Water by Chromous Salts, and their Use for the Absorption of Oxygen.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 127, 24—27).—Since the oxidation of chromous chloride, with production of the oxychloride,  $\text{Cr}_2\text{Cl}_4\text{O}$ , is accompanied by the evolution of a larger amount of heat ( $100.4 \text{ Cal.}$ ) than is produced in the formation of water from its elements, there should be a tendency to the decomposition of water by chromous chloride. The latter reaction does not take place at the ordinary temperature in the case of pure solutions of chromous salts containing no free acid; above  $250^\circ$ , however, or at the ordinary temperature in presence of traces of free hydrochloric acid, decomposition slowly occurs, and hydrogen is evolved. An explanation of the influence of the hydrochloric acid in this reaction is suggested by a consideration of the properties of the green and violet modifications of chromic chloride, which are formed from chromous chloride with the evolution of  $94.6 \text{ Cal.}$  and  $113.4 \text{ Cal.}$  respectively. The oxychloride formed by the oxidation of the chromous chloride is not converted by the hydrochloric acid into the green chromic chloride, since this reaction would involve the absorption of  $5.8 \text{ Cal.}$ ; under the influence of time, however, the formation of the violet modification is rendered possible, with the evolution of  $13 \text{ Cal.}$ , and it is the supplementary energy of this reaction which determines the slow decomposition of the water.

It follows from the foregoing observations that an acid solution of chromous chloride should not be employed as an absorbent of oxygen in the exact analysis of gaseous mixtures, or in the purification of any gas but hydrogen.

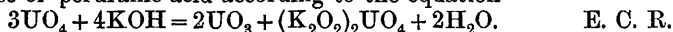
N. L.

**Peroxides.** By PETR. G. MELIKOFF and L. PISSARJEWSKY (*Zeit. anorg. Chem.*, 1898, 18, 59—65).—The authors discuss the results which they have obtained in their researches on the peroxides (Abstr., 1898, ii, 161, 165, 219, 292, 332, 337, and 374). They have

shown that the acid peroxides are capable of forming salts with alkali peroxides. The soluble salts, for example, the sodium and lithium salts of peruranic acid, when treated with aluminium hydroxide, are converted into the free acid and hydrogen peroxide; the insoluble salts, for example, the barium salt of peruranic acid, when treated with carbonic anhydride, behave like barium peroxide, and barium carbonate, hydrogen peroxide, and peruranic acid are formed.

Acid peroxides of the type  $\text{RO}_4$  have been obtained from elements belonging to six groups. The stability of the salts which they form with alkali peroxides decreases with the atomic weight of the element which forms the acid peroxide. Those peroxides which are strong acids do not form salts with metallic peroxides, but decompose the latter, with formation of hydrogen peroxide.

The authors assign to the peroxy-acids and metallic peroxides a constitution of the type of hydrogen peroxide,  $\text{HO}-\text{OH}$ , since they show a similar behaviour towards many reagents. When treated with dilute sulphuric acid, they yield hydrogen peroxide; with concentrated sulphuric acid, many of them yield ozone. The peroxy-acids are decomposed by water in a similar manner to the metallic peroxides; thus, sodium perborate is partially [decomposed into sodium metaborate and hydrogen peroxide; they also behave in a manner similar to the metallic peroxides when treated with manganese peroxide, whereby oxygen is rapidly evolved in the case of soluble salts, and slowly in that of insoluble salts. The peroxy-acids very easily oxidise alkalis, converting them into peroxides, for example, in the case of peruranic acid according to the equation



E. C. R.

**Permolybdates.** By PETR. G. MELIKOFF and L. PISSARJEWSKY (*Ber.*, 1898, 31, 2448—2451).—The failure of Muthmann and Nagel (*Abstr.*, 1898, ii, 593) to obtain potassium peroxide permolybdate having the properties described by the authors can only be due to their failure to reproduce the necessary experimental conditions, and for this reason the authors repeat their description of the method employed by them.

To a solution of potassium permolybdate prepared by Péchard's method (*Abstr.*, 1891, 988) are added aqueous solutions of potash and hydrogen peroxide (3 per cent.) in amounts corresponding with the scheme  $\text{KMoO}_4 + 3\text{KOH} + 4\text{H}_2\text{O}_2$ ; the liquid, which has now become dark red, is mixed with alcohol cooled to  $-10^\circ$  to  $-12^\circ$ , insufficient in amount to precipitate potassium peroxide. The flocculent, red precipitate thus produced is separated by means of a filter cooled by ice and salt, washed with alcohol and ether successively, and finally dried on a cooled tile. The salt thus obtained is ready for analysis, and always possesses the same properties; it evolves oxygen when dissolved in water at the ordinary temperature, changing colour simultaneously, and it is exploded by friction, or by the heat spontaneously developed on exposure to air; it is not hygroscopic as was the substance obtained by Muthmann and Nagel, and it is probable that these experimenters were dealing with an impure specimen containing potassium peroxide.

The suggestion made by Muthmann and Nagel, that the foregoing substance contained some hydrogen peroxide, is untenable, as its properties are not sensibly different if excess of hydrogen peroxide be employed in its preparation, and when it is reprecipitated from a solution in alkaline hydrogen peroxide its properties remain unaltered. It is, therefore, a chemical individual.

The authors are unable to accept the view that the molybdates can combine with a molecular proportion of oxygen at low temperatures, and believe that there is much evidence to show that the "per-" acids form salt-like compounds with the metallic peroxides. A. L.

**Action of Hydrogen on Potassium Paratungstate.** By L. A. HALLOPEAU (*Compt. rend.*, 1898, 127, 57—58).—When potassium paratungstate is heated to dull redness in a current of hydrogen, a mixture of tungsten dioxide with the blue oxide of tungsten is obtained. At higher temperatures, a compound of the composition  $K_2O.WO_3 + WO_2.WO_3$  is also produced, which crystallises in small, reddish-violet prisms having a coppery lustre. This substance, which appears to be identical with the compounds obtained by Laurent and by Wöhler, may be purified by prolonged washing with boiling water, concentrated hydrochloric acid, and potassium carbonate solution. At a bright red heat, it undergoes further reduction by hydrogen, with formation of metallic tungsten. N. L.

**Production of Tungsten Blue by the Reduction of Tungsten in Porcelain Furnaces.** By ALBERT GRANGER (*Compt. rend.*, 1898, 127, 106—107).—When a mixture of barium and sodium tetraungstates,  $M'_2O.WO_3$ , is used as a glaze on porcelain and is heated in a reducing flame at about 1250°, it yields a blue colour varying from pale blue to indigo. The tint depends on the proportion of the two salts and the quantity of the glaze used, and can also be modified by adding borax or phosphates. The blue colour is most probably due to the formation of the oxide  $W_2O_5$  in the conditions specified.

C. H. B.

**Lead-antimony, Tin-antimony, Tin-arsenic, and Tin-phosphorus Alloys.** By JOHN E. STEAD (*J. Soc. Chem., Ind.*, 1897, 16, 200—208 and 309).—When alloys of lead and antimony containing from 1—12·66 per cent. of the latter, are melted and allowed to solidify, a perfectly homogeneous product is obtained. On increasing the proportion of antimony, however, crystals of the latter separate in a nearly pure state, and rising to the surface of the cooled product form a layer of a much lighter colour than the subjacent portion. The latter has a composition corresponding with the formula  $Pb_4Sb$ , and appears to be the eutectic alloy of the two metals; it has a sp. gr. = 10·48, melts at about 247°, and solidifies in ill-defined hexagonal plates. Although all lead-antimony alloys, except the eutectic, have two critical points, one of these always corresponds with the fusing temperature of the compound  $Pb_4Sb$ .

When alloys of tin and antimony are melted and cooled, as long as the amount of the latter does not exceed 7·5 per cent., perfectly homogeneous products are obtained. On increasing the amount of

antimony, well-defined crystals separate, which consist of a combination of cubic and octahedral forms. They were isolated from the matrix by dissolving the latter completely in dilute nitric acid (sp. gr. = 1.04); thus obtained, they appear to consist of *tin antimonide*,  $\text{SnSb}$ , and have a sp. gr. = 6.96 (calc. 7.00). It appears that tin antimonide only crystallises from alloys containing an excess of tin; the crystals are formed best when 75 per cent. of the latter is present. On melting tin antimonide and allowing the mass to cool, cubic crystals are no longer formed in the solidifying mass; it appears that, like iron carbide,  $\text{Fe}_3\text{C}$ , tin antimonide is decomposed by fusion.

On melting alloys of tin and phosphorus containing from 0.04—5 per cent. of the latter, brilliant, white, crystalline plates of *tin phosphide*,  $\text{Sn}_3\text{P}_2$ , separate on cooling; this was isolated by the same process as was used for preparing tin antimonide. It is decomposed when heated in a stream of hydrogen, phosphine being formed, whilst spontaneously inflammable hydrogen phosphide is evolved when any of the tin-phosphorus alloys are acted on by concentrated hydrochloric acid.

A crystalline *tin arsenide* was isolated by the author from alloys of arsenic and tin; it separates from the still molten tin at a temperature of  $530^\circ$ , and apparently has the composition  $\text{Sn}_3\text{As}_2$ . W. A. D.

**Oxidation of Aluminium in Contact with Mercury.** By H. F. HUNT and L. J. STEELE (*J. Soc. Chem. Ind.*, 1896, 15, 849—850).—When aluminium is allowed to stand on mercury covered with a thick film of oxide, although apparently no amalgamation takes place, the aluminium is rapidly converted into its hydroxide. The action is not so rapid when the metal is kept beneath dirty mercury, and is very slight when aluminium is floated on freshly distilled mercury. The hydroxide is formed most rapidly on aluminium which has had its surface amalgamated by the ordinary methods. W. A. D.

**A Chloriodide of Tin.** By C. LENORMAND (*J. Pharm.*, 1898, [vi], 8, 249—253).—Although iodine does not act on anhydrous stannous chloride at the ordinary temperature, it combines with it, when heated at  $100^\circ$  for several hours, forming *tin chloriodide*,  $\text{SnCl}_2\text{I}_2$ . This is a mobile, red liquid, which fumes in the air, and has a sp. gr. = 3.287 at  $15^\circ$ ; it is decomposed by water, and when poured into ether or ethylic, propylic, butylic, or amylie alcohol, gives rise to a crystalline compound. When tin chloriodide (100 grams) is heated, it begins to distil at  $191^\circ$ , but the temperature gradually rises to  $297^\circ$ ; the residue (55.44 grams) in the flask at this temperature consists of nearly pure *stannic iodide*,  $\text{SnI}_4$ . If the distillate obtained be redistilled, a further quantity of stannic iodide is left, and still more can be isolated by repeating the process. Ultimately, 67.78 per cent. of stannic iodide and 26.82 per cent. of stannic chloride were obtained; the *total* result of the decomposition can therefore be expressed by the equation  $2\text{SnCl}_2\text{I}_2 = \text{SnCl}_4 + \text{SnI}_4$ . W. A. D.

**Double Sulphates of Antimony and the Alkali Metals.** By AUGUST GUTMANN (*Arch. Pharm.*, 1898, 236, 477—479).—*Antimony potassium sulphate*,  $\text{KSb}(\text{SO}_4)_2$ , prepared by dissolving antimonic oxide

in a boiling solution of potassium sulphate in concentrated hydrochloric acid, crystallises in small, six-sided, nacreous leaflets. The corresponding *sodium* salt forms small, scaly crystals, and the *ammonium* salt large, glistening leaflets. A. W. C.

**Action of Heat on the Double Rhodium-Alkali Nitrites.** By ALEXANDRE JOLY and EMILE LEIDIÉ (*Compt. rend.*, 1898, 27, 103—106). —The double nitrites of rhodium with potassium, sodium, and barium begin to decompose at about 360°, but the products at this temperature are complex and indefinite. If, however, the salts are heated in a vacuum between 440° and incipient redness until evolution of gas ceases, and the products are then treated with water, definite, insoluble, crystalline compounds are obtained. The potassium salt yields the compound  $K_2O, 6RhO_2$ , the sodium salt the compound  $Na_2O, 8RhO_2$ , and the barium salt the compound  $BaO, 12RhO_2$ . These compounds are to be regarded as the salts of hexarhodous acid, octarhodous acid and dodecarhodous acid respectively, and the acids are products of the condensation of rhodous acid,  $H_2O, RhO_2$ . The existence of these compounds affords definite evidence of the existence of an oxide,  $RhO_2$ , with an acidic function; they are analogous to the chromites, cobaltites and manganites obtained by G. Rousseau, and their formation seems to show that the production of salts of peroxides by the action of heat on double nitrites is a property common to many of the metals of the platinum group. C. H. B.

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## Mineralogical Chemistry.

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**Cedarite, an Amber-like Resin from Canada.** By RICHARD KLEBS (*Jahrb. f. Min.*, 1898, ii, 212; from *Jahrb. k. preuss. geol. Landesanst.*, for 1896, 1—32).—This resin, to which the new name cedarite is given, has been known since 1890 at Cedar Lake, near the mouth of the North Saskatchewan River, and in many other parts of Western Canada. It occurs as isolated grains in wood-bearing, alluvial beds, and appears to have been originally derived from strata of Cretaceous or Tertiary age. The grains, having sometimes the form of drops, are rarely as large as a pea, and never exceed a walnut in size. The resin is clear yellow, but sometimes brown and cloudy. The sp. gr. is that of amber, but the hardness rather less. Analysis gave

C.	H.	S.	O.	Ash.	Total.
78.15	9.89	0.31	11.20	0.45	100.00

It is only partially soluble in alcohol, ether, acetone, &c. Melting point  $340^{\circ}$ ; at  $390^{\circ}$  it decomposes and leaves a residue of 86.8 per cent. of colophony. Succinic acid is absent. It is of much less commercial use than Baltic amber. Other fossil resins are compared with the one here described. [This mineral (formerly called chemawinite) has already been described, *Abstr.*, 1892, 573].

L. J. S.

**Uintahite (Gilsonite) Deposits of Utah.** By GEORGE H. ELDRIDGE (*Jahrb. f. Min.*, 1898, ii. Ref. 211; from 17th *Ann. Rept. U.S. Geol. Survey*, 1896, part i, 909—949).—Uintahite or gilsonite is an asphalt, occurring abundantly in the Uintah mountains of Utah. It differs from albertite and grahamite in the brown or reddish-brown streak, hardness of  $2-2\frac{1}{2}$ , and sp. gr. of 1.065—1.070. It fills fissures, 1 in. to 18 ft. across, in the Tertiary beds, and has apparently been forced up from below. Analysis by W. C. Day (*J. Franklin Inst.*, 1895, 140, No. 837) gave,

C.	H.	S.	O+N.	Ash.	Total.	Volatile.	Solid residue.
88.30	9.96	1.32	[0.32]	0.10	100.00	54.46	43.43

Day considers it to be a mixture of hydrocarbons of the paraffin, and perhaps also of the naphthalene, series. L. J. S.

**Occurrence of Hydrogen Sulphide in the Natural Gas of Point Abino, Canada; Estimation of Sulphur in Gas Mixtures.** By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1898, 20, 696—705).—The gas escaping from the well at Point Abino is strongly contaminated with hydrogen sulphide, which may be proved by passing it through solutions of lead acetate or ammoniacal cadmium chloride. The gas, after being passed through lead acetate, gives no precipitate or marked odour when again passed through mercuric chloride, showing the absence of volatile sulphur compounds; palladium chloride also remains unaffected.

In order to estimate the quantity of hydrogen sulphide, the lead sulphide obtained from a definite volume of the gas was oxidised by means of hydrochloric acid and potassium chlorate, and the sulphuric acid formed estimated as barium sulphide. A more convenient way, although requiring a complicated apparatus, was found to be to pass a current of carbonic oxide through a definite volume of the gas, and then to burn the mixed gas in oxygen, the products of combustion being collected in an absorption apparatus containing sodium carbonate and some bromine. All the sulphur was thus obtained as sulphuric acid, which was then estimated in the usual way, as barium sulphate. L. DE K.

**Composition of Retzian.** By HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1898, ii, Ref. 209; from *Geol. För. Förh.*, 1897, 19, 106—112).—In the analysis of the new mineral retzian, a hydrated arsenate of manganese, calcium, &c., a constituent amounting to 10.3 per cent. (0.0082 gram) was previously not identified (*Abstr.*, 1896, ii, 35). This is now stated to be rare earths, most probably yttrium oxides with a molecular weight of about 250. The manganese and calcium, as given in the analysis, may also have contained rare earths. A formula cannot yet be given. The orthorhombic crystals have the parameters,  $a:b:c = 0.4414:1:0.7270$ . L. J. S.

**Fergusonite, an Endothermic Mineral.** By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1898, 62, 325—329).—The mineral examined gave, on analysis (by Miss Aston),

(Nb,Ta) <sub>2</sub> O <sub>5</sub>	(Y,Er,&c.) <sub>2</sub> O <sub>3</sub>	(Ce,&c.)O <sub>2</sub>	VO <sub>2</sub>	UO <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	PbO	CuO	Total
40.95	31.09	13.87	3.36	3.81	4.56	1.42	1.55	0.16	0.12	100.89

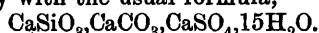
When heated to 500—600°, the mineral suddenly becomes incandescent, and liberates, per gram of mineral, He, 1.080 c.c.; H<sub>2</sub>, 0.078; CO<sub>2</sub>, 0.245; N<sub>2</sub>, 0.027; on further heating with potassium hydrogen sulphate, it yields, in addition to CO<sub>2</sub>, He, 0.733; N<sub>2</sub>, 0.088; O<sub>2</sub>, 0.394 c.c. per gram of mineral. The total percentage of helium is 0.0326. The density is 5.619 before, 5.375 after, heating to incandescence; the mean specific heat of the mineral between 0° and 17.3° is 0.1069. To determine the heat of decomposition, the mineral was heated in a platinum crucible (contained in a calorimeter) by burning under the crucible, in oxygen, a known weight of hydrogen, and noting the additional rise of temperature above that obtained when hydrogen was burned under the empty crucible. The heat of decomposition is +809 calories per gram of mineral, and is probably caused by the decomposition of an endothermic compound of helium with some constituent of the mineral.

C. F. B.

**Thaumasite from Skottvång, Sweden.** By HELGE BÄCKSTRÖM (*Jahrb. f. Min.*, 1898, ii, Ref. 196; from *Geol. För. Förh.*, 1897, 19, 307—310).—Thaumasite has recently been found at a new Swedish locality, namely, in the mines of Skottvång, parish of Gåsinge, Nyköping. It occurs as an aggregate of prismatic crystals between, and later than, crystal aggregates of apophyllite. The hexagonal prisms, are without distinct terminal faces, which are optically uniaxial and negative;  $\omega = 1.505$ ,  $\epsilon = 1.468$ . Sp. gr. 1.871—1.875. Analysis gave,

H <sub>2</sub> O.	CO <sub>2</sub> .	SiO <sub>2</sub> .	SO <sub>3</sub> .	CaO.	Total.
43.28	7.01	9.68	12.88	27.16	100.01

This agrees closely with the usual formula,



L. J. S.

**Diopside (Salite) as a Weathering Product in Palæopicrite from Medenbach (Nassau).** By REINHARD BRAUNS (*Jahrb. f. Min.*, 1898, ii, 79—88).—With a little serpentine and calcite, salite fills crevices in a palæopicrite at Medenbach, near Herborn; it is compact to fibrous, and light grey to yellowish-grey. The optical characters are those of diopside, with the extinction angle  $\epsilon:c = 40^\circ$ . Sp. gr. = 3.31. The following analysis by Noack gives the formula  $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ .

SiO <sub>2</sub> .	FeO.	MnO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Total.
55.56	3.65	trace	—	24.51	15.58	99.30

The palæopicrite is composed of olivine (mostly altered to serpentine), augite and plagioclase, with ilmenite and magnetite. In the serpentine are small, radiated groups of spear-shaped crystals of salite, which has been derived from the olivine.

L. J. S.

**Kainosite from the Ko Mine, Sweden.** By HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1898, ii, Ref. 202; from *Geol. För. Förh.*, 1897, 19, 54—60).—Only one Norwegian crystal of this mineral, kainosite or cenosite, has previously been known. It has now been found in



small, isolated crystals associated with clinocllore and apatite in a druse consisting mainly of magnetite and diopside at the Ko mine, Nordmark. The crystals, which do not exceed 2 mm. across, are yellowish-brown or dark chestnut-brown; they are opaque and have a feeble vitreous to greasy lustre,  $H = 5-6$ ; there is no distinct cleavage. The short, prismatic crystals are orthorhombic, with the forms  $\{110\}$ ,  $\{001\}$ , and  $\{011\}$ , and others less prominent. The parameters,  $a:b:c = 0.9517:1:0.8832$ , are compared with those of cerite. The mineral is easily soluble in hydrochloric acid with evolution of gas ( $\text{CO}_2$ ?). Analysis by R. Mauzelius, on 0.0666 gram, gave

$\text{SiO}_2$	$\text{Y}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	Alkalis.	$\text{H}_2\text{O}$	$\text{CO}_2$	Total.	Sp. gr.
31.7	35.9	2.9	16.5	1.4	3.6	2.9	[5.1]	100.0	3.38

With the  $\text{Fe}_2\text{O}_3$  is possibly some  $\text{BeO}$ , and other elements may be present. This composition agrees with that of the Hitterö mineral.

Yttrium minerals usually occur in pegmatite veins and in other separations from ancient eruptive rocks; and an occurrence in an ore deposit is remarkable.

L. J. S.

**Minerals [Hessonite, &c.] from the Urals.** By ALEKSANDR N. VON KARNOJITSKY (*Zeit. Kryst. Min.*, 1898, 30, 311—319; from *Verh. k. russ. min. Ges.*, 1896, [ii], 34, 1—160).—The new Eugenie-Maximilianow mines, 15—20 km. west and north-west of Ekaterinburg, yield the following minerals, many of them as fine crystals: garnet (hessonite, &c.), epidote (very abundant), sphene, axinite, clinocllore, microcline, idocrase, beryl, corundum, &c. These are, in nearly all cases, confined to the junction of the orthoclase rocks (granite and syenite), and the amphibole rocks (gneiss, &c.), but they also rarely occur in dolomite at the dolomite-granite contacts. The following analyses are given of hessonite. I. Fine, transparent rhombic-dodecahedral crystals, often 3—4 cm. across, light yellow to dark-reddish in colour, from Mt. Pup. II. Transparent yellowish to orange-red crystals from Mt. Mjedwjeschka. III. Greyish-yellow crystals from the same locality. Analyses I, II by W. Alexéeff, III by W. Worobióff.

	$\text{SiO}_2$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MnO}$	$\text{MgO}$
I.	39.10	0.50	17.75	6.50	35.77	trace	0.19
II.	38.10	0.78	16.30	10.53	35.00	trace	trace
III.	39.3	0.4	17.9	6.3	35.5		1.3

All the crystals of hessonite show optical anomalies, the lighter coloured being the most strongly birefringent, whilst the darker are sometimes almost isotropic. The difference in colour, depending on the amount of iron, is also connected with a difference in optical orientation.

L. J. S.

**[Mariposite.]** By HENRY W. TURNER (*Jahrb. f. Min.*, 1898, ii, Ref. 200; from 17th *Ann. Rept. U.S. Geol. Survey*, 1896, part i, 678—679; and *Amer. J. Sci.*, 1895, 49, 377).—Mariposite was described by Silliman in 1868 as a green, micaceous mineral from the gold-quartz veins of Tuolumne and Mariposa counties, California. It is abundant

at the Josephine mine, near Beau Valley. Analyses by Hillebrand gave I for the green, sp. gr. = 2·817; and II for the white, sp. gr. = 2·787. Water is not given off below 300°. In thin sections, both are nearly colourless: they show bright polarisation colours, and give straight, or nearly straight, extinction.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	MgO	K <sub>2</sub> O	(Li,Na) <sub>2</sub> O	H <sub>2</sub> O
I.	55·35	0·18	25·62	0·18	0·63	0·92	0·07	3·25	9·29	0·12	4·52
II.	56·79	25·29	Nil		1·59		0·07	3·29	8·92	0·17	4·72

No definite formula can be given, and the material appears to be similar to pinite. L. J. S.

**Marekanite-obsidian from Nicaragua.** By JOHANNES PETERSEN (*Jahrb. f. Min.*, 1898, ii, 156—159).—Marekanite balls from Corinto in Nicaragua are described; they are about the size of hazel-nuts, and black, with vitreous lustre. They are difficult to break with a hammer, but when cut they fly to pieces; in form, they are approximately spheres or truncated pyramids, and the surfaces show concave areas. Under the microscope, fragments of the transparent, colourless glass show flow structure marked out by numerous globulites, trichites, and small crystals. These marekanite balls appear to be perlite balls rather than the kernels of perlitites, as has been supposed, and a rock composed of them may be called a marekanite-obsidian. As shown by the following analysis, the composition is that of a liparite magma.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
	76·68	14·49	1·09	trace	0·84	1·53	1·20	3·92	0·36	100·11

L. J. S.

**Dyke Rocks from Adamello Mountains.** By CARLO RIVA (*Jahrb. f. Min.*, 1898, ii, Ref. 247; from *Atti Soc. Ital. Sci. Nat.*, 1897, 27, 265).—Numerous dyke rocks, mostly intersecting the tonalite, have recently been found in the Adamello Mountains, on the Italian-Tyrol border; they include diorite-porphyrites, vintlites, malchites, odinites, and aplites. Analysis I is of malchite, with hornblende and biotite, from the Passo di Campo; II, of malchite, with augite and biotite, from Lago d'Arno. Both are grey to grey-brown rocks with felspar (andesine-labradorite) and quartz. They are more basic than the surrounding tonalite.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O	Total
I.	57·48	16·82	8·49	4·64	5·45	2·63	4·57	0·25	100·33
II.	56·77	20·02	6·40	3·70	5·40	4·01	3·94	0·13	100·36

L. J. S.

**Analysis of the Mineral Water of Castrocaro.** By FAUSTO SESTINI and R. CAMPANI (*L'Orosi*, 1897, 20, 43—47).—The results of the analysis of this mineral water are given below in tabular form. The sp. gr. = 1·0312 at 15°. The total volume of the gases expelled from one litre by boiling is 50·15 c.c., including CO<sub>2</sub>, 29·94 c.c.; O<sub>2</sub>, 4·39 c.c.; N<sub>2</sub> (gas unabsorbed by potash or phosphorus), 15·80 c.c.

Substance.	Grams per litre.	Substance.	Grams per litre.
Cl .....	36·8109	Na <sub>2</sub> O .....	28·0284
Br.....	0·1382	CaO.....	2·2047
I.....	0·1516	MgO.....	1·2676
SO <sub>3</sub> .....	0·5845	Fe <sub>2</sub> O <sub>3</sub> .....	0·0014
SiO <sub>2</sub> .....	0·0219	Organic matter.....	0·6842
P <sub>2</sub> O <sub>5</sub> .....	0·0026		

Total solid residue dried at 180° = 61·7475. A series of monthly analyses made during the year 1891—1892 show that the composition of the water is fairly constant; there is, however, a marked decrease in the amounts of bromine and iodine, more especially the former, in the rainy months of the year.

N. L.

**The Sulphur Water of Sandefjord.** By EYVIND BÖDTKER (*Annalen*, 1898, 302, 43—51. Compare Strecker, *Annalen*, 1855, 95, 177).—The Sandefjord is in the neighbourhood of Christiania, and opens into the Skager Rack. Water drawn from the spring there is a transparent, yellowish liquid having a powerful odour of hydrogen sulphide; owing to separation of sulphur, it becomes turbid on exposure to the air, but clear again after a long interval. The liquid is neutral, but acquires alkaline properties if kept in glass bottles, black sulphide of iron separating during the change. On July 19, 1893, the temperature of the spring was 10·3° at half-past eleven, identical with that observed by Strecker towards the end of June, 1853; if the temperature is raised above this point, carbonic anhydride is liberated. The amount of solid matter dissolved in the water is very variable, and appears to fluctuate between 1·5 and 3 per cent. The quantity of hydrogen sulphide in 1000 c.c. is, on the other hand, fairly constant; it amounted to 34·26 c.c. in the summer of 1892, and 37·89 c.c. a year later. A complete analysis of the gaseous and solid substances dissolved in the water is given in the paper, showing that the quantities of carbonic anhydride and hydrogen sulphide have increased by 33 per cent. and 60 per cent. respectively during the last 50 years.

The *gytje* is a peculiar, dark grey mud which collects in sheltered bays along this coast. At Sandefjord the *gytje* is greasy to the touch, and has the odour of hydrogen sulphide; it is used for mud baths. A specimen, dried at 100°, gave the following results on analysis.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	NaCl.	KCl.	K <sub>2</sub> SO <sub>4</sub> .	CaO.	Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> .	MgO.	FeO.
54·43	12·93	5·57	0·65	2·11	1·89	0·37	1·64	4·88

with organic matter (9·87), and chemically combined water 5·97, making the total 100·31. One thousand parts by weight of the moist substance contained 1·53 and 0·083 parts of ammonia and hydrogen sulphide respectively.

The water in the fjord itself, observed by Strecker to contain only 1·40 per cent. of salts, now contains almost twice this amount.

M. O. F.

## Physiological Chemistry.

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**Composition of Normal Gastric Juice.** By ADOLF SCHÜLE (*Chem. Centr.*, 1898, i, 347, from *Zeit. klin. Med.*, 33, 543—546).—A case is described in which gastric juice was obtainable free from saliva; it contained some flakes of mucin; the free hydrochloric acid varied from 0.09—0.2 per cent.; the sp. gr. = 1.0012. The peptonising power of 3 c.c. was 50—55 per cent. (Hammerschlag's method); the juice did not invert cane-sugar, neither did it give the xanthoproteic reaction, nor the tests for albumoses or peptone. W. D. H.

**Influence of Organic Foods on Inorganic Metabolism.** By ANGELO PUGLIESE (*Chem. Centr.*, 1898, i, 266—267; from Du Bois Reymond's *Archiv*, 1897, 473—485).—On the administration of carbohydrates and fats to dogs, the excretion of nitrogen and phosphates sinks; gelatin also causes a fall in the phosphates excreted. Sugar and, to a less degree, fat and gelatin, produce a rise in the output of sodium and potassium, the alkaline earths, however, not being affected. The total quantity of urine is lessened by feeding with sugar, but increased by intravenous injection of sugar. Very small quantities of sugar increase the output of nitrogen and phosphates. W. D. H.

**Oxidation of Acetone and Homologous Fatty Ketones [in the Organism].**—By LEO SCHWARZ (*Chem. Centr.*, 1898, i, 264; from *Arch. exp. Path. Pharm.*, 40, 168—194).—The separation of acetone is chiefly effected by the lungs. With doses of 0.2 to 1.6 grams per kilogram weight of the animal, 1—4 per cent. is found in the urine, and when larger quantities are administered, proportionately greater amounts are thus separated. Since very small quantities of acetone are not completely oxidised in the body, acetone cannot occur as an intermediate product of physiological action, and neither albumin nor carbohydrates yield acetone when oxidised with potassium permanganate. The power of oxidising acetone in dogs is not diminished by inducing diabetes in them by means of phloridzin, or by extirpation of the pancreas, but the organism is then able to form acetone from acetoacetic acid, whereas in the healthy animal acetoacetic acid, hydroxyisobutyric acid,  $\beta$ -hydroxybutyric acid, and mesityl oxide do not yield acetone. In the healthy organism, however, acetone is formed from acetoxime, and the mixed ketones of the fatty series are partly oxidised and partly excreted. Of the ketones examined, diethyl ketone is physiologically the most easily oxidised. E. W. W.

**Presence of Manganese in Minerals, Plants, and Animals.** By P. PICHARD (*Compt. rend.*, 1898, 126, 1882—1885).—Manganese seems to be universally diffused in rocks, plants, and animals. The author gives a list of 36 orders of plants, including both phanerogams and cryptogams, in which he has detected this element by the method previously described. It seems to be concentrated in the leaves and

other parts of the plant that are in active growth, and especially in the seeds of phanerogams.

The proportion of manganese in animals is much smaller than in plants. It is noteworthy that the yolk of an egg contains much more than the white, an egg contains more than flesh, and flesh contains more than bones.

C. H. B.

**Comparative Chemistry of the Suprarenal Capsules.** By B. MOORE and SWALE VINCENT (*Proc. Roy. Soc.*, 1898, 62, 352—354).—The suprarenal capsules of teleostean fishes resemble, anatomically, the inter-renal body of elasmobranchs, and the cortex of mammalian suprarenals. The chromogen present in the medulla of mammalian suprarenals is absent, and extracts of the teleostean capsules are physiologically inactive. No organ corresponding to the medulla is found in these fishes.

W. D. H.

**Presence of Organic Chlorine in Normal Urine.** By DIOSCORIDE VITALI (*L'Orosi*, 1897, 20, 114—119; 145—153).—The question of the existence in urine of chlorine in various forms of combination is discussed, and an account is given of the experiments which have hitherto been made with a view to distinguishing between the chlorine present as chlorides and that existing in intimate combination with organic substances and incapable of being directly precipitated by silver nitrate. The results obtained by previous observers are criticised in detail, and sundry discrepancies therein are shown to be due to defective methods of analysis. That "organic chlorine" exists in urine to a small, but not insignificant, extent, is demonstrated by the following process, which appears to be free from sources of error. The urine is rendered distinctly acid with pure nitric acid, a slight excess of silver nitrate added, and the liquid filtered from the precipitated silver chloride. The excess of silver in the filtrate is removed by hydrogen sulphide, the liquid filtered, warmed to expel hydrogen sulphide, filtered again, mixed with potassium nitrate and excess of sodium carbonate, evaporated to dryness in a platinum dish, and incinerated. The residue is extracted with water, and to the filtered solution, after acidification with nitric acid, silver nitrate is added; the precipitate thus obtained is soluble in ammonia, but insoluble in boiling concentrated nitric acid, and does not, therefore, consist of silver cyanide, as has been suggested by some experimenters. Some experiments made with the object of ascertaining the nature of the organic chlorine compounds in urine, showed that they are not extracted from acid or alkaline urine by ether, chloroform, or light petroleum.

N. L.

**Phosphorus in Urine.** By LEOPOLD JOLLY (*Compt. rend.*, 1898, 127, 118—119).—Sometimes urine contains phosphorus in a form that is not precipitated even by a large excess of ammoniacal magnesium mixture, and this phosphorus has been supposed to exist in an incompletely oxidised form (Lépine and Aubert), or as phosphoglyceric acid. The author finds, however, that the urine of many patients suffering from nervous disorders or diathesia, and even the urine of healthy persons after an excess of food, contains peculiar nitrogen compounds which are not affected by the ordinary reagents for

albumins and peptones, but are precipitated by tannin and by concentrated mercuric chloride solution. These nitrogen compounds retain some metallic phosphates in such intimate association that the phosphoric acid in them is not precipitated by magnesium mixture, and the author considers that it is these phosphates, and not phosphoglyceric acid or any incompletely oxidised form of phosphorus, that escapes precipitation by the ordinary method. C. H. B.

**Elimination of Chlorides in Rachitis.** By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1898, 127, 72).—The urine in five cases of rachitis was found to contain chlorides (calculated as sodium chloride?) ranging from 11.22 to 12.14 grams per litre. These results, corresponding with a considerable loss of chlorine, are in accordance with the author's views as to the nature of the disease. N. L.

**Proteose in Urine.** By HEINRICH ROSIN (*Chem. Centr.*, 1898, i, 74—75; from *Berlin. Klin. Woch.*, 34, 1044—1047).—In a female patient suffering from myelogenic sarcoma of the thoracic skeleton, a proteose resembling in general characters deutero-albumose was present in the urine. W. H. D.

**Chemistry of Amyloid Degeneration.** By N. P. KRAWKOFF (*Chem. Centr.*, 1898, i, 261—262; from *Arch. exp. Path. Pharm.*, 1897, 40, 195—220).—The author describes the occurrence of chondroitinsulphuric acid in healthy and diseased men and animals. The amyloid substance is prepared from the various organs, the liver, kidneys, and spleen, from which the Glisson's capsule and the larger vessels have been removed, by treating them in small pieces with cold water and a dilute solution of ammonia. The mass is macerated on a nickel gauze sieve, and washed with dilute ammonia until the filtrate is free from chondroitinsulphuric acid. After washing with water, it is digested for several days with pepsin-hydrochloric acid, the mass then treated with ammonia, in which the greater part dissolves, and the amyloid precipitated with hydrochloric acid. The flocculent precipitate is washed with water, alcohol, and ether. The product contained C, 46.92; H, 6.60; N, 14.16, and P, 1.16 per cent. The phosphorus is due to the presence of nucleins which may be removed by treating the freshly-precipitated substance with baryta water. The amyloid gives the reaction with methyl-violet, but the reaction with iodine is dependent on its physical condition. Analyses of four preparations are quoted. The amyloid is insoluble in weak alkalis, and is a combination of chondroitinsulphuric acid with an albuminous substance; by the action of pepsin-hydrochloric acid, the latter is possibly converted into an albumose complex. In healthy organisms, the amyloid occurs so sparsely distributed in the walls of arteries, that the colour reactions are not apparent. E. W. W.

**Pharmacology of Aconitine, Diacetylaconitine, Benzaconine, and Aconine.** By J. THEODORE CASH and WYNDHAM R. DUNSTAN (*Proc. Roy. Soc.*, 1898, 62, 338—347).—*Action on the Circulation.*—Aconitine first stimulates the medullary centres, slowing the heart; acceleration follows, auricles and ventricles taking up an independent rhythm. Imperfect systole and delirium of the ventricles may

follow. If the poisoning is slow, stimulation of the cardiac vagus ceases to produce the usual inhibitory effect. The vaso-motor centre is first stimulated, then depressed.

Diacetylaconitine produces in the main the same results, but in a less marked manner.

Benzaconine produces a preliminary acceleration of the pulse, and then slowing, with fall of blood pressure, ensues; this is due to the depression of the motor mechanism within the heart. The vaso-motor centre is depressed. Vagus stimulation causes slowing until a late stage of the poisoning is reached. Digitaline is an effective antagonist.

Aconine is comparatively harmless.

*Action on Respiration.*—Aconitine first stimulates, then depresses, the respiratory centre and the pulmonary sensory vagal fibres.

Diacetylaconitine produces a slighter initial stimulation; death results from central failure. Respiratory spasm occurs at death.

Benzaconine depresses the centres from the first. Respiratory failure is partly produced by act on on motor nerve endings, and causes death without spasm.

Aconine slows the respiration, and has a pronounced curare-like action on the motor nerve endings.

*Action on the Nervous System.*—Aconitine produces no distinct narcotic effect, but the depression is secondary to diminution of oxidation processes from cardiac and respiratory failure. There is preliminary stimulation. Sensation is depressed.

Diacetylaconitine produces a similar, but less marked, effect.

Benzaconine causes a semi-narcotised condition, which is partly referable to low intracranial pressure. Sensory nerves are but little affected.

Aconine produces loss of volition in large doses.

*Action on Oxidation.*—Tested with vegetable protoplasm, all reduce oxidation processes, aconitine being the most, and aconine the least, active. All produce a fall of body temperature in the same order of activity.

*Lethal Doses.*—These are stated in fractions of a gram per kilo. of body weight for cat, rabbit, guinea-pig, and frog. The figures for the cat are:

Aconitine .....	0.000134
Diacetylaconitine .....	0.004 to 0.005
Benzaconine .....	0.0245
Aconine .....	0.16 to 0.4

*General Conclusions.*—The introduction of two additional acetyl groups into the molecule of aconitine slightly weakens, but does not materially modify, its action. The removal of the acetyl group so as to form benzaconine almost entirely annuls its characteristic actions. The withdrawal of the benzoyl group (as in aconine) reduces the toxicity still more. In fact, aconine and benzaconine are largely antagonistic to aconitine.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

**Action of the Sorbose Bacterium on Xylose (Wood-sugar).** By GABRIEL BERTRAND (*Compt. rend.*, 1898, 127, 124—127).—When the bacterium of sorbose is allowed to grow in a decoction of yeast mixed with xylose, the latter is slowly, but almost completely, converted into xylonic acid.  
C. H. B.

**Composition of the Mycelium of Mould Fungi.** By MARSHALL (*Bied. Centr.*, 1898, 27, 575; from *Arch. Hyg.*, 28, 16—29; and *Chem. Centr.*, 1897, i, 115).—Analyses were made of *Aspergillus niger*, *Penicillium glaucum*, and *Mucor stolonifer* before fructification. The average percentage composition of the dry matter was found to be as follows.

Proteids.	Ether extract.	Alcohol extract.	Cellulose.	Starch.	Nitrog. extract sol. in water.	Ash.
38	5.27	14.03	5.03	2.8	28.47	6.37

The fungi occupy, therefore, as regards composition, a position between bacteria and the higher plants.  
N. H. J. M.

**Germination.** By F. VICTOR JODIN (*Ann. Agron.*, 1898, 24, 382—390. Compare *Abstr.*, 1898, ii, 129).—Experiments similar to those previously described were made with dead pea seeds, sterilised and not sterilised. The sterilised seeds remained practically inert, whilst the results obtained with the non-sterilised seeds seemed to indicate very active respiration. On repeating the experiment with live peas, the relation  $\text{CO}_2/\text{O}_2$  was 1.00 with sterilised, and 1.23 with non-sterilised seeds, showing that the activity of live seeds is able to overcome the effect of microbes.

Pea seeds, seven years old, the germinative power of which was very much weakened, were covered with water. They did not germinate, but underwent a slight change, liberating carbonic anhydride and absorbing oxygen.

Cotyledons (of peas), after removal of the rudimentary plant, continued to give off carbonic anhydride, and retained a great part of the chemical energy of the seeds. But the nature of the change was entirely altered. Thus whilst during two successive periods of 5 days the relation,  $\text{CO}_2/\text{O}_2$ , was 1.41 and 0.84 with entire peas which had germinated normally, it was 14.08 and 2.15 in the case of the mutilated peas.  
N. H. J. M.

**Effect of Formaldehyde on the Germination of Sugar Beet Seed.** By ANTON STIFT (*Bied. Centr.*, 1898, 27, 568; from *Oesterr. Zeit. Zuckerind.*, 1898, i.).—Beetroot seeds retained, without exception, their power of germinating, after remaining 24 hours in an atmosphere of formaldehyde (compare Windisch, *Abstr.*, 1898, ii, 40).  
N. H. J. M.



**The Presence of Simple Organic Compounds in the Vegetable Kingdom.** By ADOLF LIEBEN (*Monatsh.*, 1898, 19, 333—354).—It has previously been shown (*Abstr.*, 1895, ii, 348) that the only product which can be isolated when carbonic anhydride is reduced with nascent hydrogen is formic acid. Experiments have now been undertaken to determine whether grass and the leaves of different trees yield formic acid or other volatile products when mixed with their own weight of acidified water (containing about 0·6 per cent. of sulphuric acid) and then subjected to distillation with steam. The faintly acid distillates were treated with sodium hydrogen carbonate and evaporated to dryness, and the solid residue examined for different acids. In all cases, formic and acetic acids, and a higher fatty acid, probably propionic, were obtained, the amount of acetic acid being greater than that of the other acids, although the amounts were invariably small; for example, from 72 kilos. of grass only 11 grams of the mixed barium salts were obtained. A small quantity of a higher crystalline acid was isolated which was practically insoluble in water, readily soluble in ammonia, fused readily, and gave insoluble lead and silver salts.

The neutral volatile products were obtained by distilling with steam and attaching a fractionating column to the flask; the distillate coming over was examined separately, and then the column was removed, the distillation continued, and the distillate examined for acids. Methylic and ethylic alcohols and a small quantity of oil were the only neutral products isolated, the amount of ethylic alcohol being always greater than that of methylic, and experiments indicated that this alcohol was only obtained after the vegetable tissue had remained for some time in contact with water.

In order to determine whether the acid and neutral products thus obtained were actually present in the leaves, &c., or were obtained by the action of the acidified water on the carbohydrates present in the tissues, the author subjected cane-sugar to an exactly similar treatment, and it was found that neither methylic nor ethylic alcohol was formed, but, apparently, when 5 or 10 per cent. sulphuric acid was employed, a small quantity of furfuraldehyde was produced. The volatile acids obtained from different carbohydrates, for example, filter paper, starch, and cane-sugar, were formic acid and a small quantity of a higher solid acid, probably identical with that obtained from leaves.

When cane-sugar was mixed with water acidified with tartaric acid and then subjected to distillation with steam, formic acid was the only volatile product isolated.

J. J. S.

**Physiological Meaning of Phosphoric Acid in the Organism of Sugar Beet.** By JULIUS STOKLASA (*Bied. Centr.*, 1898, 27, 537—539; from *Zeit. Zuckerind. Böhmen*, 1897, 403, and *Oesterr. Zeit. Zuckerind. u. Landw.*, 1897, 933).—Of the total phosphoric acid in beet seeds, 2·72 is in the form of lecithin. In seedlings six days old (sand-culture), the amount of phosphoric acid as lecithin was 6 per cent. of the total, and after 30 days, 9 per cent. was found in the leaves and stems, and 4·6 per cent. in the roots. In the case of plants grown under ordinary conditions, 6·3 per cent. of the phosphoric acid of the leaves

was present as lecithin after 60 days, but only 5 per cent. in the roots. At the end of the vegetative period, when the outer leaves were yellow, the green leaves contained 0·89, and the yellow leaves only 0·15, per cent. of lecithin.

The dry substance of chlorotic beet contained only 0·22 per cent. of lecithin, whilst green leaves contained nearly 1 per cent. in the dry matter.

As leaves die off and the chlorophyll is destroyed, the lecithin migrates to the root, where it is stored up, chiefly in the head, presumably in anticipation of second year's growth. N. H. J. M.

**Chlorophyll in a Nostoc grown in the Dark.** By ALEXANDRE ÉTARD and BOULHAC (*Compt. rend.*, 1898, 127, 119—121).—A *Nostoc* grown in the dark on a solution of glucose containing certain salts, was found to contain a green chlorophyll, which gave the spectrum characteristic of the glaucophylls found in ordinary living leaves, except that the band  $\lambda 548-536$  had a much higher relative intensity than usual, being stronger than the band  $\lambda 631-606$ , although not so strong as the band  $\lambda 690-650$ . The alcoholic solution was yellowish-green with a distinct red fluorescence. Whether this chlorophyll possesses the ordinary chlorophyllien function was not ascertained. C. H. B.

**Conditions of Development and the Composition of the Volatile Mustard Oils of the Seeds of the Cruciferæ.** By GUNNER JØRGENSEN (*Bied. Centr.*, 1898, 27, 697—699; from *Tidskr. f. Fysik. og Kemi. Copenhagen*, 1898, 3, 91—111).—The investigation was undertaken in consequence of the poisoning of cattle fed with rape cake. The cakes examined, which were stated to be rape cake, proved in some cases to consist of *Brassica napus* or *B. rapa*, in other cases the seeds of *Sinapis*, *Eruca* and *Erysimum* were found. Various *Brassica* seeds, unmixed, were also examined.

The cakes which acted corrosively on the digestive organs of the cows, did not show any considerable difference in the amount of mustard oil they produced. The composition of the mustard oils from different sources varied, however, considerably. In some cases (*Sinapis nigra* and *Brassica juncea*) the analytical results corresponded with the composition of allylthiocarbamide; in other cases (*Brassica glauca*, *B. dichotoma* &c.), the thiosinamine produced was a crotonylthiocarbamide.

The permanence of the pungent odour, produced by stirring with water and adding white mustard, was fairly proportional to the amount of "Indian seeds" in the cakes. Under the conditions of the experiments (the substance 5, mustard 1, water 100 grams, were kept at 40° in a closed 250 c.c. flask), the odour of mustard oil could still be detected after from 0—2 hours when no Indian rape was present, after 18—19 hours when the sample consisted mainly of Indian rape, after 26 hours with *sarepta*, and after 28 hours with black mustard.

N. H. J. M.

**Microchemical Proof of the Presence of Alkaloids in Medicinal Drugs.** By HERMANN BARTH (*Arch. Pharm.*, 1898, 236, 354—367).—The paper contains the results of a number of experiments made on some drugs with the idea of determining in which cells or

cell-complexes the alkaloids are to be found. In addition to the ordinary reagents, the following were often found to give good results:—vanadium sulphate, a sulphuric acid solution of cerium sulphate, and selenium sulphate and nitrate.

Some reagents, such as iodine, bromine, chlorine, hydrochloric and nitric acids, were employed in the form of vapour, thus permitting the use of a very powerful reagent, without dilution. Such reagents are strong enough to kill the plasma and convert the alkaloid, combined with an organic acid into an easily crystallisable salt. Many alkaloids for example, give crystalline substitution or additive products with the halogens, which are, however, easily soluble in water. Such compounds can, in the above manner, be easily detected by the microscope, or at all events when a polarising microscope is employed, as most of them are doubly refractive.

The results, which cannot well be abstracted, lead the author to the belief that the alkaloids are utilised during the germinating and development of the young plants, which is in agreement with Heckel's views (compare *Arch. Pharm.*, 1892, 555). A. W. C.

**Formation of Proteids in Plants by the Reduction of Nitrates.** By ALEXANDRE HÉBERT (*Ann. Agron.*, 1898, 24, 416—440).—The results of different investigators indicate that in the reduction of nitrates in plants, hydrogen cyanide is formed, and that this action usually takes place in those organs in which chlorophyll is present, and where the production of formaldehyde also predominates. After calling attention to the great combining power, and the facility of forming polymerides, which formaldehyde possesses, and the similar properties of cyanogen derivatives, it is suggested as probable that the two substances combine in the vegetable cells, yielding the more or less complex nitrogen compounds which form the fundamental products of the hydration of albumin.

N. H. J. M.

**Amount of Nitrogenous Substances other than Proteids in Ripe Straw and Chaff.** By PAUL HOLDEFLEISS (*Bied. Centr.*, 1898, 27, 532—534; from *Habilitationsschr. Halle a-S.*, 1897).—The total nitrogen, and the pure proteids (by Stutzer's method) were determined in a large number of samples of the straw and chaff of various plants. The following is a summary of the percentage results relating to non-proteids:

	Cereals.				Leguminous.			
	Straw.		Chaff.		Straw.		Chaff.	
	Total.	In total proteids.	Total.	In total proteids.	Total.	In total proteids.	Total.	In total proteids.
Lowest ..	0	0	0·049	3·49	0·058	5·39	0·078	6·05
Highest..	0·102	15·74	0·117	13·23	0·203	19·37	0·465	24·49
Mean ....	0·049	7·29	0·085	8·19	0·123	11·74	0·244	12·25

N. H. J. M.

**Amount of Nicotine in Retail Cigars and Tobacco.** By HUGO SINNHOLD (*Arch. Pharm.*, 1898, 236, 522—529).—The amount of nicotine in European cigars, varies from 0.648 to 2.957 per cent. and in Havanna cigars from 0.972 to 2.241 per cent. Cigarette tobaccos contain 0.801 to 2.887 per cent., and pipe tobaccos 0.518 to 1.854 per cent. of nicotine.

The analytical methods employed were those of Kissling (*Zeit. anal. Chem.*, 21, 64; 22, 199), and Popovici (*Diss. Erlangen*, 1889).

A. W. C.

**The Changes in Sugar when Stored.** By LEOPOLD JESSER (*Bied. Centr.*, 1898, 27, 701—705; from *Oesterr. Zeit. Zuckerind.*, 1898, 35). **Behaviour of Raw Sugar when Stored.** By N. RYDLEWSKI (*ibid.*, from *D. Deut. Zuckerind.*, 1897, 1413, and *Oesterr. Zeit. Zuckerind.*, 1897, 1202).—Raw sugar in quantities of 1 cwt., contained in sacks, was buried in sugar. The sacks were taken out from time to time, in order to obtain samples, in which the cane-sugar and the alkalinity were determined.

The results agree with those of previous investigators, in showing that the changes which sugar undergoes are not due to the composition of, at any rate, the normal non-sugars present, but to micro-organisms. The change does not progress uniformly. High alkalinity does not prevent the change, but when neutrality is reached reducing substances are produced in such amounts that they can be determined by ordinary methods.

In the early stages of decomposition, analysis is unable to decide whether the sugar is likely to change much or little when stored. As a rule, strongly alkaline sugar can be kept longest. Feebly alkaline sugar, however, is often well able to resist change, especially when sulphurous acid has been employed.

N. RYDLEWSKI stored different sugars for 100, 200, and 300 days, and examined them by the usual methods. He concludes that there is no danger as long as the sugar shows an alkaline reaction. The preparation of the sugar, for example, with or without animal charcoal, has no effect if the alkalinity of the sugar amounts to 0.020 or 0.030.

N. H. J. M.

**Production of Humus from Manures.** By HARRY SNYDER (*Agr. Expt. Stat. Univ. Minnesota Bul.*, 53, 1897, 12—35. Compare *Abstr.*, 1898, ii, 449).—Cow manure, green clover, and meat scraps produce valuable, highly nitrogenous humus, capable of combining with the phosphoric acid and potash of the soil. Sawdust, straw, and carbohydrates produce humus rich in carbon, which has less power to combine with the phosphoric acid and potash of the soil than the more nitrogenous forms of humus.

Prolonged cropping produces less nitrogenous and more carbonaceous humus as compared with the humus of uncultivated land.

Forest fires may dissipate 75 per cent. of the total nitrogen of the soil, and the practice of burning over new land sometimes causes permanent injury to the soil.

Soils which are deficient in humus are sandy and sandy-loam soils, which have grown maize, potatoes, and small grains without application of stable manures or without the proper rotation of crops.

Prairie soil contains, per acre, about 1500 lbs. of phosphoric acid

and 800 lbs. of potash combined with humus. After twenty years of cultivation, the amount of phosphoric acid is reduced to about 400 lbs. if the supply of humus is not kept up. N. H. J. M.

**Production of Nitrogenous Manure.** By JOSEF KÖNIG (*Bied. Centr.*, 1898, 27, 667—671; from *Neue Zeit. Rübenzuckerind.*, 1898, 1).—Attention is directed to the possibility of supplying a great portion of the nitrogen required in Germany for manuring, in the form of ammonium salts from gas-works and coke-furnaces. It is estimated that at least 230,000 tons of ammonium sulphate, containing 46,000 tons of nitrogen, could be produced annually as against 19,600 tons actually produced in 1898.

As regards the prevalent idea that nitrogen in the form of ammonia is less valuable than in the form of nitrates, it is pointed out that, whilst for spring manuring nitrates are preferable to ammonium salts (as most plants probably assimilate nitrogen in the form of nitrates), nitrates have the disadvantage that they are liable to give rise to the formation of a crust on the surface of the soil; they are also unsuited for autumn manuring owing to loss by drainage, and when used in large amounts they injure the quality of the crops.

The application of ammonium salts involves, in the case of soils poor in lime, more or less frequent addition of marl, lime, or basic slag; marl and ammonium salts may be applied simultaneously, but should be at once ploughed in.

Experiments have shown the relative values of ammonium sulphate and sodium nitrate to be 90—95 : 100. But when the disadvantages of sodium nitrate are taken into account, both forms of nitrogen may be considered equal. N. H. J. M.

**Assimilation of Nitrates, and the Effect of Different Nitrates.** By W. SCHNEIDEWIND (*Bied. Centr.*, 1898, 27, 674—676; from *J. Landw.*, 1898, 46, 1).—The results of experiments with sugar-beet manured with sodium and potassium nitrates respectively, indicated that the sodium salt gave a greater yield of dry matter and sugar in the roots, whilst the potassium salt produced a greater amount of leaf. The better effect of sodium nitrate is attributed to its greater solubility and diffusibility.

In the case of oats manured with various nitrates, the yield of grain was greatest with the magnesium salt; sodium nitrate gave the next largest amount of grain, then calcium, and, lastly, potassium nitrate. Magnesia has a special rôle in the production of grain; but it is supposed that the better result of sodium as compared with potassium nitrate is due, as in the case of sugar-beet, to the greater solubility of sodium salts, and to the consequent more rapid supply of nitrogen and phosphoric and sulphuric acids to the plant. Straw production was least with magnesium, and greatest with potassium nitrate.

The composition of the grain did not vary to any extent, except in the case of the magnesia plants, the grain of which was somewhat richer in magnesia. Most of the magnesia, however, was deposited in the straw.

It is not supposed that sodium can in any way replace potassium in its functions connected with the migration of starch and sugar.

N. H. J. M.

**Experiments on the Effect of the Phosphoric Acid of Bone Meal.** By JULIUS KÜHN (*Bied. Centr.*, 1898, 27, 527—530; from *Deut. landw. Presse*, 1897, 24, Nos. 62 and 63).—Bone meal, being sparingly soluble, is not very effective when applied for crops which occupy the land for short periods. Even the after-effect in such cases is inconsiderable, as, with ordinary soils, the phosphoric acid of bone meal remains, after the harvest, unchanged in the sparingly soluble, tribasic form. The effect is, however, essentially different in the case of crops such as winter wheat, perennial clovers, &c., and the appropriative power of plants such as winter rye is of importance.

Pot experiments were made, in which summer rye was grown in poor, sandy soil, without phosphate and with different amounts of various phosphates. The numbers given below show the percentage increase in produce over the unmanured pot. The amounts of phosphoric acid are given in kilos. per hectare :

	50 kilos. $P_2O_5$ .		100 kilos. $P_2O_5$ .		200 kilos. $P_2O_5$ .		400 kilos. $P_2O_5$ .	
	grain.	straw.	grain.	straw.	grain.	straw.	grain.	straw.
Superphosphate.....	15	13	45	34	—	—	—	—
Basic slag.....	61	50	79	72	—	—	—	—
Degelatinised bone meal.	64	61	—	—	—	—	—	—
Steamed bone meal .....	45	50	58	46	76	58	77	60

With heavy soils, and with crops of long vegetative periods, it is best to employ superphosphate. With good, warm, average soil, both steamed bone meal and superphosphate may be used, whilst superphosphate alone should be applied to cold loams, or cold sandy loams. In the case of good sandy soil, superphosphate should not be used; both basic slag and steamed bone meal are suitable.

There will, perhaps, in future, be more competition between degelatinised bones and basic slag for light sandy soils than has hitherto been the case.

N. H. J. M.

**Observations as to whether the Beneficial Action of Lime on the Soil of the Experiment Station is due to any extent to its Neutralising Action.** By HOMER J. WHEELER, GEORGE M. TUCKER, and BURT L. HARTWELL (*Ann. Rep. Agr. Expt. Stat. Rhode Island*, 1896, 9, 294—318).—The injurious effect which invariably resulted from the continuous application of ammonium sulphate to the soil of the Experiment Station could be overcome by simultaneous application of sufficient potassium carbonate, wood ashes, air-slacked lime, sodium carbonate, or caustic magnesia. Magnesium sulphate gave less satisfactory results, and the same holds, in a more marked degree, in the case of gypsum as compared with slacked lime. In experiments with

potatoes, gypsum failed to produce the beneficial effect observed with calcium carbonate, acetate, and oxalate, slacked lime and wood-ashes. Calcium acetate and oxalate are no doubt converted in the soil into carbonate (compare Schmoeger, *Ber.*, 1879, 755). It is concluded that, apart from the beneficial effect, both physical and manurial, of the above-named substances, they were probably, to a great extent, useful owing to a natural deficiency of bases in the soil and also in correcting acidity. Calcium chloride exerted a poisonous action (on potatoes).

N. H. J. M.

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## Analytical Chemistry.

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**Measurement of Gases.** By OTTO BLEIER (*Ber.*, 1898, 31, 2513).—The author finds the method recently described by him (*Abstr.*, 1898, i, 183) for the absolute measurement of gases has been previously used by Hempel (*Verhdlg. Vereins. Beförd. Gewerbf.*, 1894, 460).  
A. H.

**Crystals in Blowpipe Beads.** By WILHELM FLORENCE (*Jahrb. f. Min.*, 1898, ii, 102—146).—A systematic account is given of the results obtained on heating various substances in borax and sodium phosphate beads with or without the presence of lead oxide; numerous figures are given of the crystals characteristic for each element so treated. The method is recommended for the microchemical determination of minerals in the dry way.  
L. J. S.

**Use of Ferrous Salts in Alkaline Solution as a Reducing Agent in Volumetric Analysis.** By ANDRÉ JOB (*Compt. rend.*, 1898, 127, 59—60).—A solution made by adding an excess of sodium pyrophosphate to a solution of ferrous ammonium sulphate, is recommended as an alkaline reducing agent in volumetric analysis. When titrated with iodine or potassium permanganate, an operation which should be carried out in a current of hydrogen, the liquid remains colourless up to the end point, which is extremely sharp.

A solution of sodium pyrophosphate readily dissolves ferrous sulphide, and the green solution thus obtained is well adapted for the colorimetric estimation of small quantities of iron. The reaction is stated to be as delicate as that with potassium thiocyanate. The solution to be tested for traces of iron is mixed with a few drops of sodium pyrophosphate solution and one bubble of hydrogen sulphide passed in.  
N. L.

**Estimation of Moisture in Invert-sugar.** By LEONARD T. THORNE and E. H. JEFFERS (*J. Soc. Chem. Ind.*, 1898, 17, 114—116).—In consequence of the difficulty of drying invert-sugar in the ordinary way, it is usual to take the specific gravity (at 60° F.) of a 10 per cent. solution of the sample, and divide the excess of gravity over that of water (taken as 1000) by 0.386. This gives the percentage of dry sugar in the solution and the moisture in the sample is obtained by



difference. When a notable amount of mineral matter is present this is estimated, the percentage is multiplied by 0.8, and deducted from the original excess gravity before calculating out the dry sugar (Heron).

To obtain a direct method of estimating the moisture, the authors have devised an apparatus for drying the sugar at 65—70° in a slow current of carbonic anhydride at a pressure of 50—80 mm. of mercury. For this purpose, the sugar is weighed on to the end of a coil of paper contained in a test tube (previously dried until constant in weight) and is then distributed over the paper by the addition of a few c.c. of water, with certain precautions. The test tube is then placed in a wider tube which is heated in the vapour of boiling methylated spirit, and whilst kept exhausted as completely as possible by a powerful and constantly working exhaust pump, a very slow current of carbonic anhydride is allowed to pass through the apparatus. The results agree very closely with those deduced from the specific gravity of the solutions provided that the ash is weighed after sulphating and  $\frac{1}{20}$  deducted before multiplying by 0.8; also for invert-sugars, the factor 0.3888 given by Brown, Morris and Millar (*Trans.*, 1897, 80), is employed instead of 0.386, which is the correct factor for saccharose.

M. J. S.

**Use of a Solution of Phloroglucinol-vanillin for the Detection of Halogens in Organic Compounds.** By P. N. RAIKOW (*Chem. Zeit.*, 1898, 22, 20—21).—An alcoholic solution of phloroglucinol-vanillin has been successfully used for the detection of free hydrochloric acid in gastric juice; the author now states that it may be successfully applied to test for halogens in the products of combustion of organic substances.

The safest way is to operate as follows. A porcelain dish is rinsed with some of the reagent and then dried; a little of the substance to be tested is burnt on a platinum wire in a spirit lamp, or, if it is a gas, it is either burnt from a jet, or a current of it is passed through the spirit flame. If the dish coated with the reagent is inverted over the flame, the least trace of halogen acid formed will be indicated by the intensely red permanent coloration.

L. DE K.

**Estimation of Oxygen in Copper.** By MAURICE LUCAS (*J. Pharm.*, 1898, [vi], 8, 311—312).—By varying the details of the silver nitrate method of estimating cuprous oxide in copper, the author has determined the conditions which are necessary to give concordant results agreeing with those obtained on reduction by hydrogen. It appears, also, that when cuprous oxide alone is treated, the amount of copper in the residue corresponds with that required by Hampe's equation, and that the action of silver nitrate on mixed cuprous oxide and copper gives the same result as its action on the separate components of the mixture. On immersing a sheet of copper in a neutral solution of copper nitrate, no precipitate containing copper is obtained on filtering.

W. A. D.

**Estimation of Sulphur in Coal.** By GEORGE L. HEATH (*J. Amer. Chem. Soc.*, 1898, 20, 630—637).—The author rejects, for technical

purposes, those processes which are based on fusing with an oxidising mixture, as this involves an evaporation in order to render any silica insoluble.

The best method is the one proposed by Eschka, provided that bromine is used as the oxidising agent; the details are as follows. One gram of the powdered coal is intimately mixed with 1 gram of pure light magnesia and half a gram of dry sodium carbonate, and heated in a 100 c.c. platinum dish with the flame of a large spirit lamp, at first very slowly; the mixture is frequently stirred with a platinum wire, and the whole is finally heated for 15 minutes at a low, red heat. When cold, the contents are transferred to a beaker, and boiled for 5 minutes with 100 c.c. of water and 15 c.c. of saturated bromine water; the filtrate is finally mixed with a slight excess of hydrochloric acid and then precipitated with barium chloride, with the usual precautions.

L. DE K.

#### Estimation of Traces of Hydrogen Sulphide in the Air.

By KARL B. LEHMANN (*Chem. Centr.*, 1898, i, 139; from *Arch. Hyg.*, 30, 262).—*First method.*—Eight litres of air are drawn through 10 c.c. of N/100 iodine solution, at the rate of 6 litres in 30 minutes, by means of an aspirator, any traces of iodine which may be carried off by the current being caught in a trap containing an N/100 solution of sodium thiosulphate. From the loss in iodine, the amount of hydrogen sulphide is calculated.

*Second method.*—The same volume of air is passed through a glass tube 30 cm. long and 12 mm. wide containing a strip of filter paper 5 cm. long and 2 cm. wide which has been saturated with lead nitrate solution. If the paper turns pale yellowish-brown, the air contains about 1·4—2 parts of hydrogen sulphide per million; if dark brown, the amount will be from 3—5 parts, and if brownish-black, 8 or more parts may be present.

L. DE K.

**Titration of Combined Sulphuric Acid.** By MAX REUTER (*Chem. Zeit.*, 1898, 22, 357).—The author has tried Andrews' process (*Amer. Chem. J.*, 1880, 2, 567), and finds that it gives excellent results if the titration with thiosulphate is made in a liquid containing only 5 c.c. of hydrochloric acid instead of 20; as this necessitates a longer contact with potassium iodide, the beaker should be covered with a watch-glass, and the air kept off by a surface current of carbonic anhydride.

The process, as will be remembered, consists in precipitating the sulphuric acid by means of a solution of barium chromate in hydrochloric acid. The excess of barium chromate is then removed by means of calcium carbonate, and the filtrate which contains an amount of soluble chromate equivalent to the sulphate is acidified with hydrochloric acid, mixed with potassium iodide, and titrated with sodium thiosulphate.

L. DE K.

#### Estimation of Nitrogen by the Kjeldahl-Gunning Method.

By K. WEDEMEYER (*Chem. Zeit.*, 1898, 22, 21).—The author has proved by a number of experiments that the addition of potassium sulphate, as recommended by Gunning, to the usual mixture of sulphuric acid,

phosphoric anhydride, and metallic mercury, considerably shortens the time of boiling without in the least interfering with the accuracy of the method.

NOTE.—Those who have read Gunning's original Dutch paper know that his chief object was to obviate the addition of potassium permanganate, salts of heavy metals, phosphoric anhydride, &c. L. DE K.

**Detection of Nitrates in Milk by means of Formaldehyde.** By E. FRITZMANN (*Chem. Centr.*, 1898, i, 218—219; from *Zeit. Öffl. Chem.*, 3, 610—614).—Nitrates, which, if present in milk, are a sure sign of the presence of adulteration with water, may be detected by adding to the milk a small quantity of formaldehyde, such as one drop of a 40 per cent. solution to 250 c.c. of the sample. On adding strong sulphuric acid, which should be chemically pure, a blue ring is obtained, and, on shaking, the liquid turns reddish- or bluish-violet. Too much formaldehyde interferes with the reaction; if, therefore, the reaction still shows when more of it is added, the amount of nitrates is considerable. L. DE K.

**Estimation of Phosphoric Acid.** By HENRI LASNE (*Compt. rend.*, 1898, 127, 62—64).—According to Vignon (*Abstr.*, 1898, ii, 639), the sum of the amounts of phosphoric acid precipitated as ammonium magnesium phosphate from the solutions obtained by treating superphosphate, (1) with water, (2) with ammonium citrate solution, is always considerably less than the amount precipitated from the mixture of the two solutions. The author, in his large experience of superphosphate analysis, has never observed such a discrepancy, and quotes the results of three experiments in support of his opinion of the exactitude of the precipitation of phosphoric acid in presence of ammonium citrate. It is also maintained that ammonium magnesium phosphate is absolutely insoluble in a liquid containing one-third of its volume of ammonia of 22°, and experiments are described which show that even as little as a milligram of phosphoric acid in a litre of liquid is completely precipitated as the double salt. N. L.

**Estimation of Phosphoric Acid.** By LÉO VIGNON (*Compt. rend.*, 1898, 127, 191).—A reply to Lasne (preceding abstract). The author does not dispute the fact that the phosphoric acid soluble in citrate solution may be determined with accuracy directly, but maintains that his method of estimating it by difference offers the combined advantages of rapidity and accuracy. N. L.

**Estimation of Phosphoric Acid for Physiological Purposes.** By ALBERT NEUMANN (*Chem. Centr.*, 1898, i, 219—223); from *Du Bois Reymond's Arch.*, 1897, 552—553).—The destruction of the organic matter is effected by means of strong sulphuric acid and ammonium nitrate, 1 gram for every c.c. of the acid, the operation being conducted in a Kjeldahl flask and the substance introduced in two or three separate portions. To destroy the organic matter in 25 c.c. of urine, 10 c.c. of acid is required; for 25 c.c. of milk or 8 grams of fresh meat, 15 c.c.; and for 5 grams of dry fæces, 20 c.c. of acid is needed.

The phosphoric acid is then estimated gravimetrically or, if possible, by the volumetric uranium process. L. DE K.

**Method of Preparing a Strictly Neutral Ammonium Citrate Solution.** By A. D. COOK (*J. Amer. Chem. Soc.*, 1898, 20, 585—586).—Seven hundred and forty grams of citric acid is placed in a 4-litre measure containing 1900 c.c. of 10 per cent. ammonium hydroxide, the mixture is vigorously stirred until it is all dissolved, and the solution made up to the mark; after being again well stirred, it is transferred to a large porcelain evaporating dish and allowed to remain overnight; in the morning it will be found to be perfectly neutral both to corallin and cochineal. It is then diluted with water to a sp. gr. = 1.09 at 20°. L. DE K.

**Estimation of Citrate Soluble Phosphoric Acid in Bone Meals, Superphosphates, &c.** By O. BÖTTCHER (*Chem. Zeit.*, 1898, 22, 201—202).—Five grams of the sample is repeatedly ground up with a solution of ammonium citrate containing free citric acid, and the whole introduced into a Stohmann's half-litre flask, which is then filled up to the mark with the citrate solution at 17.5°. After closing the flask with an indiarubber cork, it is rotated for 30 minutes in a suitable apparatus which turns 30—40 times per minute round its axis. The liquid is then filtered and 50—100 c.c. is used for the estimation of the phosphoric acid either by the molybdic or the magnesia method.

**Preparation of the Citrate Solution.**—One hundred and fifty grams of citric acid is put into a litre flask, dissolved in water, and exactly neutralised with ammonia; 10 grams of citric acid is then added, and the whole is made up to 1 litre. Before use, 1 volume of the solution is diluted with 4 volumes of water. L. DE K.

**Ignition of Magnesium Ammonium Phosphate.** By HUGO MASTBAUM (*Zeit. anal. Chem.*, 1898, 37, 581—582).—With reference to the rapid method of igniting magnesium ammonium phosphate described by Schmöger (*Abstr.*, 1898, ii, 455), the author states that even the preliminary drying of the precipitate is unnecessary, but that the wet precipitate, wrapped in its paper filter, may be placed in the platinum crucible and the latter at once exposed to the full flame of a Bunsen burner. The water assumes almost instantly the spheroidal condition, and no loss of precipitate takes place. After 15—20 minutes, the grey residue is moistened with strong nitric acid, which is then carefully evaporated. Exposure to the blowpipe flame for half a minute completes the ignition. M. J. S.

**Volumetric Analysis of a Mixture of Alkyl Phosphates with Phosphoric Acid.** By JACQUES CAVALIER (*Compt. rend.*, 1898, 127, 60—61).—The composition of a mixture of phosphoric acid with the two alkyl phosphates,  $\text{RH}_2\text{PO}_4$  and  $\text{R}_2\text{HPO}_4$ , where R is methyl, ethyl, or allyl, may be determined volumetrically by a process based on the behaviour of these compounds towards different indicators and on the different solubilities of the barium salts. The dialkyl hydrogen phosphate is acid to methyl-orange and to phenolphthalein, and is rendered neutral to both indicators by combination with one equivalent of alkali. The monalkyl dihydrogen phosphate is neutralised by one

equivalent of alkali if methyl-orange is used as the indicator, and by two equivalents if phenolphthalein is employed; the barium salt is soluble in water. Phosphoric acid resembles the preceding compound in its behaviour with indicators, but the barium salt,  $\text{BaHPO}_4$ , is insoluble in water. The mixture of the three acids is first titrated with baryta water in the cold, using methyl-orange as indicator, and the liquid is then warmed to about  $60^\circ$  and the titration completed to the end point indicated by phenolphthalein. The first titration gives the sum of the three acids and the second the two polybasic acids,  $\text{RH}_2\text{PO}_4$  and  $\text{H}_3\text{PO}_4$ . The liquid is now filtered from the precipitated barium hydrogen phosphate, and both precipitate and filtrate are mixed with excess of standard hydrochloric acid. The phosphoric acid and the monalkyl dihydrogen phosphate respectively contained in the two solutions thus obtained are then titrated with baryta water, the volume of alkali required to pass from the end point indicated by methyl-orange to that indicated by phenolphthalein being determined. The sum of the two results should be equal to that given by the second titration of the original mixture.

N. L.

**Separation and Estimation of Arsenic.** By JOHN PATTINSON and HUGH S. PATTINSON (*J. Soc. Chem. Ind.*, 1898, 17, 211—214).—Arsenious sulphide requires for dissolution not more than 400,000 parts of hydrochloric acid of sp. gr. = 1.17 saturated with hydrogen sulphide. In the absence of hydrogen sulphide, the solubility is somewhat greater, although still very minute. Lead, cadmium, tin, antimony, and bismuth are not precipitated at all by hydrogen sulphide from acid of this strength, and the separation of arsenic from these metals is quantitatively complete. The precipitate may be washed with a mixture of 5 parts of hydrochloric acid and 2 parts of hydrogen sulphide solution without loss, and without risk of precipitation of the other metals. If the arsenic be in the form of arsenic acid, it may be reduced by stannous chloride before passing the gas.

The arsenious sulphide is best collected on an asbestos (Gooch) filter. After washing with acid, and then completely with water, it may either be weighed, or, if the quantity amounts to only a few centigrams, it may be heated with 10—15 c.c. of strong sulphuric acid in an uncovered beaker at a temperature at which the acid gives off white fumes. No loss of arsenic is to be feared if chlorides are absent. Hydrogen sulphide is first given off, then sulphurous anhydride; the acid darkens at first but becomes colourless when all the sulphurous anhydride is expelled. A clear solution of arsenious acid is thus obtained. The solution is then nearly neutralised with sodium hydroxide, rendered alkaline with excess of sodium hydrogen carbonate, and titrated with iodine. A blank experiment with the same sulphuric acid is desirable. Very accurate results are obtained.

M. J. S.

**Volumetric Estimation of Boric Acid.** By VADAM (*J. Pharm.*, 1898, [vi], 8, 109—111).—In presence of an excess of mannitol, the quantity of boric acid present in a solution can be determined by adding decinormal caustic soda until an alkaline reaction with phenol-

phthalein or litmus is obtained; the end point of the reaction is more sharply defined than in Barthe's method, using glycerol (*Abstr.*, 1896, ii, 337). In both cases, however, 1 c.c. of decinormal alkali is equivalent to 0.0062 gram of boric acid. The above method is available for determining boric acid in butter; 1.5 grams of the latter is extracted with warm water (20 c.c.), the free fatty acids present neutralised with decinormal caustic soda in presence of litmus, 1—2 grams of mannitol added, and the boric acid determined as above described.

W. A. D.

**Estimation of Potassium.** By JULIUS DIAMANT (*Chem. Zeit.*, 1898, 22, 99).—The author, finding a great difficulty in making potassium platinochloride perfectly anhydrous, now proposes the following process.

The double salt, which should weigh about 0.5 gram, is dissolved in boiling water in a 500 c.c. flask, and when cold is diluted to the mark, and 1 gram of zinc dust is added; this rapidly decomposes the compound, forming zinc and potassium chlorides. Two hundred and fifty c.c. is then pipetted off and titrated with N/10 silver nitrate; from the chlorine thus found, the amount of potassium chloride may be readily calculated.

L. DE K.

**Test for the Presence of Sodium Hydrogen Carbonate in Sodium Carbonate.** By MELCHIOR KUBLI (*Arch. Pharm.*, 1898, 236, 321—324).—The test for the presence of sodium hydrogen carbonate in sodium carbonate, as given in the *Pharmacop. German.*, III., and in the *Pharmacop. Ross.*, IV., is not sufficiently delicate, as, according to the author, it will not show the presence of 2 per cent. of the acid salt, and according to Thümmel (*Pharm. Central-H.*, 1891, 86) as much as 4—5 per cent. may escape detection. The author therefore proposes the following test, which depends on the fact that an aqueous solution of a soluble quinine salt of a certain concentration is not precipitated by normal sodium carbonate, if the latter does not contain more than 2 per cent. of sodium hydrogen carbonate.

Ten c.c. of a solution of quinine hydrochloride, containing 0.4 gram of the salt in 100 c.c. water, is added to 10 c.c. of the sodium carbonate solution (3 grams in 50 c.c. water); if there is not more than 2 per cent. of sodium hydrogen carbonate present, no permanent cloudiness is produced. The quinine solution should be preserved from air and light.

A. W. C.

**Estimation of Perchlorate in Chili Saltpetre.** By OTTO FOERSTER (*Chem. Zeit.*, 1898, 22, 357).—Ten grams of the sample is mixed with 10 grams of pure dry sodium carbonate and heated in a covered platinum or porcelain dish over the full flame until the fused mass flows quietly; this takes about 10 minutes. When cold, the mass, which can be readily detached from the dish, is dissolved in dilute nitric acid, and the total chlorine titrated by Volhard's method; after allowing for chlorine present in other forms, the difference is calculated to perchlorate.

L. DE K.

**Estimation of Lead in Ores.** By FR. MOLDENHAUER (*Chem. Zeit.*, 1898, 22, 256—257).—Two grams of the finely powdered ore is boiled

with strong hydrochloric acid until hydrogen sulphide is no longer evolved; if much antimony is present, this may be practically expelled by evaporating to dryness two or three times with strong hydrochloric acid; the addition of a little nitric acid is advisable. The dry residue is now moistened with hydrochloric acid, 100 c.c. of water is added, the liquid boiled to dissolve the lead chloride, and the insoluble matter repeatedly washed with boiling water until quite free from lead; 300 c.c. generally suffices. The filtrate, heated to redissolve any deposited lead chloride, is nearly neutralised with ammonia, precipitated with hydrogen sulphide, and the lead sulphide collected, washed, and digested with ammonium sulphide. It is then treated, together with the paper, with nitric acid, evaporated to dryness, and after being heated to expel any sulphur and organic matter, is converted into sulphate by means of sulphuric acid; finally, the sulphate is freed from other metals by washing, dried, and weighed.

L. DE K.

**Estimation of Traces of Lead in Water.** By A. LIEBRICH (*Chem. Zeit.*, 1898, 22, 225).—One, or more, litres of water is concentrated, acidified with acetic acid, precipitated with hydrogen sulphide, and the precipitate ignited and converted into sulphate by heating with a drop of sulphuric and nitric acid. The lead sulphate is then dissolved in a few c.c. of 10 per cent. aqueous potash, diluted to 20 c.c., mixed with 2 c.c. of freshly prepared ammonium sulphide, and the tint compared with that given by a standard solution of lead sulphate in aqueous potash containing 1 milligram of lead per c.c., and also diluted to 20 c.c. The experiment is then repeated, using more, or less, of the standard lead. By way of control, the lead sulphide may be again converted into sulphate and weighed.

L. DE K.

**New Volumetric Method for the Estimation of Copper.** By RICHARD K. MEADE (*J. Amer. Chem. Soc.*, 1898, 20, 610—613).—The solution of the copper ore is evaporated with sulphuric acid, the residue is dissolved in water, the greater part of the free acid neutralised with ammonia, and sulphurous acid added in excess; the copper is then precipitated by adding a slight excess of ammonium thiocyanate. The precipitate, collected on asbestos, is well washed and then put back into the beaker, where it is heated with aqueous (3 per cent.) potash; the suboxide thus produced is again collected on an asbestos filter, well washed with hot water, and then heated in a beaker with solution of pure ferric sulphate until it is entirely dissolved. The cuprous oxide sets free a corresponding equivalent of ferrous oxide, which is then titrated with permanganate, the iron equivalent of the permanganate multiplied by 1.125 giving the weight of the copper in the sample.

Instead of sulphurous acid, a mixture of equal weights of sodium hydrogen sulphite and potassium thiocyanate may be used to precipitate the copper. Ferric chloride may be used instead of ferric sulphate, but the titration with permanganate is then less safe. The process is not interfered with by the presence of arsenic, antimony, bismuth, or zinc.

L. DE K.

**Estimation of Copper in Vegetables.** By VICTOR VEDRÖDI (*Chem. Zeit.*, 1898, 22, 103—104).—This is a controversy with Lehmann on the subject of the occurrence of copper in vegetable substances. The author (*Abstr.*, 1897, ii, 602) has found in the same samples a very much larger amount of copper than Lehmann did, and attributes this to the inaccuracy of the latter's colorimetric process. The author also expresses his view that the presence of even 0·8 gram of copper per kilogram of wheat does not constitute a danger to health, as the metal is there in the form of a harmless compound.

L. DE K.

**Estimation of Copper in Vegetable Substances.** By KARL B. LEHMANN (*Chem. Zeit.*, 1898, 22, 296—297).—A reply to Vedrödi (preceding abstract). The author cannot understand the great differences in the amount of copper found by Vedrödi and himself in the ash of the same cereals, but he upholds his own views.

L. DE K.

**Estimation of Cuprous Oxide by Permanganate.** By ROBERT M. CAVEN and ALFRED HILL (*J. Soc. Chem. Ind.*, 1897, 16, 981—983; 17, 124).—Cuprous oxide dissolves completely and rapidly in a mixture of potassium permanganate and sulphuric acid, with formation of cupric sulphate and corresponding reduction of the permanganate. One part of sulphuric acid is diluted with 3 parts of water, and 4 volumes of this acid is added to 1 vol. of standard permanganate. The cuprous oxide, collected and washed on an asbestos filter, is introduced into a measured excess of this mixture, and after stirring for a minute or two the unreduced permanganate is titrated with oxalic acid. Highly satisfactory results are obtained with great rapidity.

M. J. S.

**Quantitative Separation of Metals by Hydroxylamine and Hydrazine.** By PAUL JANNASCH (*Ber.*, 1898, 31, 2377—2394).—[With G. DEVIN.]—Mercury may be separated from copper, bismuth, lead, cadmium, arsenic, antimony, or tin, in solutions of their salts, by the employment of an ammoniacal solution of hydroxylamine. A mixture of mercuric chloride and a salt of one of these metals is dissolved in water, or in hydrochloric acid if necessary, tartaric acid, ammonia, and hydroxylamine hydrochloride are added in excess, and the solution heated until the precipitation of mercury is complete; the latter is then collected, redissolved in fuming nitric acid, the solution evaporated to dryness, the residue taken up with hydrochloric acid and water, and the mercury precipitated as sulphide. From the ammoniacal filtrate, the remaining metal may be separated by suitable means, the copper as cuprous thiocyanate, the bismuth, lead, cadmium, antimony, and tin as sulphides, and the arsenic as magnesium ammonium arsenate. The copper, cadmium, bismuth, and tin are finally weighed as oxides, the lead as sulphate or peroxide, and the antimony as sulphide or oxide.

[With F. ALFFERS.]—In a similar manner, mercury is separated from molybdenum or tungsten by ammoniacal hydroxylamine in the presence of tartaric or citric acids; the precipitated metal is treated as described above, whilst from the filtrate the molybdenum is obtained as sulphide and weighed as trioxide.



The separation of mercury from aluminium, chromium, or manganese is effected by the same reducing agent in the presence of oxalic acid; aluminium and chromium are obtained as oxides, whilst the manganese is precipitated from the ammoniacal filtrate by hydrogen peroxide and weighed as the protosesquioxide. Tartaric or citric acid may be substituted for oxalic acid in the case of these metals, but its use is less convenient.

Mercury and cobalt are separated by the addition of ammoniacal hydroxylamine to the slightly acid solution of their salts, the cobalt being precipitated as sulphide in the filtrate from the mercury.

Mercury and nickel are similarly separated in the presence of an organic acid such as tartaric or citric. Either of these acids or oxalic acid may be employed in the separation of mercury from uranium by ammoniacal hydroxylamine, the latter element being determined by evaporating the filtrate to dryness, igniting, and weighing both as  $U_3O_8$  and  $UO_2$ .

[With WILHELM HEIMANN.]—Selenium, either in the form of selenious or selenic acid, is separated from sulphuric and phosphoric acids by boiling their solutions with excess of hydroxylamine hydrochloride, the selenium being precipitated and weighed, whilst the sulphuric and phosphoric acids in the filtrate are determined in the usual way. The separation of tellurous or telluric acids from sulphuric or phosphoric acids is effected in the same way.

[With M. MÜLLER.]—An ammoniacal solution of hydroxylamine reduces tellurous and telluric acids, causing the complete precipitation of the tellurium, whilst an acid solution of this reagent is without action on these acids; hydroxylamine may therefore be employed in separating selenium and tellurium. The selenium is completely precipitated when a hydrochloric acid solution of these elements is boiled with hydroxylamine, and the tellurium separates quantitatively when the filtrate is rendered ammoniacal and boiled with more of the reducing agent; four molecules of hydroxylamine are required for the reduction of one molecule of selenious acid, water and nitrogen being produced at the same time.

Tellurium is separated from palladium by distilling an alloy of these elements in a current of bromine, the tellurium bromide is volatilised and received in hydrochloric acid, and the solution reduced with ammoniacal hydroxylamine; the residue containing the palladium is dissolved in aqua regia, the metal precipitated as sulphide, and finally weighed as  $PdO_2$  and also in the metallic state.

Selenium is most conveniently separated from barium by means of hydroxylamine. Barium selenite dissolved in hydrochloric acid is boiled with excess of the reducing agent, and the selenium is collected and weighed; the barium remains in the filtrate and is estimated as sulphate.

[With M. MÜLLER.]—Hydrazine sulphate reduces selenium compounds even more energetically than hydroxylamine and precipitates selenium both from hydrochloric and nitric acid solutions.

Tellurium is also precipitated from its hydrochloric acid solution by this reagent but not from the solution in nitric acid; from a hot ammoniacal solution, hydrazine precipitates it quantitatively, and the

reduction of this element from its salts by hydrazine and by hydroxylamine is being employed in the determination of its atomic weight.

G. T. M.

**Detection of Cobalt in the Presence of Nickel.** By ADAM JAWOROWSKI (*Chem. Centr.*, 1898, i, 144; from *Pharm. Zeit. Russ.*, 36, 632—634).—The liquid, if containing free acid, is neutralised with sodium carbonate, and solid sodium pyrophosphate is added until the turbidity at first produced has again disappeared; the liquid, after being poured off from any undissolved pyrophosphate, is, if necessary, diluted with water until nearly colourless, and 6—8 c.c. of this solution is shaken with 1—1.5 grams of sodium carbonate and 5—8 drops of bromine water; if cobalt be present, even in traces, the liquid will be of a beautiful green when observed in reflected light.

L. DE K.

**Oxidation of Cobalt Salts in Presence of Alkalis.** By ANDRÉ JOB (*Compt. rend.*, 1898, 127, 100—103. Compare McConnell and Hanes, *Trans.*, 1897, 584).—It is well known that when hydrogen peroxide or bromine is added to a solution of potassium hydrogen carbonate mixed with a cobalt salt, the pink colour of the solution changes to green, but the composition of the green compound has not hitherto been ascertained. By titration with the special ferrous reagent proposed by the author (this vol., ii, 51), he finds that the ratio of cobalt oxide to active oxygen is  $2\text{Co} : \text{O}$ . Hence the green compound is a derivative of the oxide  $\text{Co}_2\text{O}_3$ ; its exact formula is  $\text{Co}_2(\text{OH})_4(\text{HCO}_3)_2$ .

The oxidation of the cobalt in presence of an alkali followed by the titration of the green compound with the ferrous reagent and iodine affords a rapid and very accurate means of estimating cobalt in presence of iron or nickel. Any excess of hydrogen peroxide soon decomposes or may be expelled by boiling the liquid for a few minutes.

The best plan is to add the solution containing the cobalt salt to a mixed solution of potassium hydrogen carbonate and hydrogen peroxide, heat gently for a few minutes and then titrate.

C. H. B.

**Analysis of Swedish Magnetic Iron Ores.** By TH. WETZKE (*Chem. Centr.*, 1898, i, 144; from *Zeit. Öfftl. Chem.*, 3, 575—577).—The solution in hydrochloric acid is effected by micro-burners so as to avoid boiling, and the vessel is covered; the iron is finally titrated with permanganate, any sulphurous insoluble residue being examined by Hauffe's method. Phosphorus is best estimated by the process recommended by Meineke (*Abstr.*, 1897, ii, 157), namely, ignition of the phosphomolybdate precipitate in a Gooch crucible.

L. DE K.

**Estimation of Tin in Tin Plate.** By ROBERT JOB (*J. Soc. Chem. Ind.*, 1898, 17, 325—326).—In a 200 c.c. flask, about 100 c.c. of pure hydrochloric acid of sp. gr. = 1.2 is placed, a piece of marble weighing about 5 grams is dropped in, and the flask is closed with a perforated cork fitted with a Bunsen valve. After about 5 minutes, 4 square inches of the tin plate, from the middle of a sheet, cut into strips, is dropped into the acid, and the flask is heated until the action becomes vigorous. When the plate is nearly dissolved, another fragment of marble is added, and immediately the plate is entirely dissolved, and while

effervescence from the marble still continues, the flask is cooled as rapidly as possible to  $0^{\circ}$ . It is then filled to the mark with ice cold water, the contents mixed, and 50 c.c. of the solution titrated with iodine (1 c.c. = 0.00056 gram of tin). A fresh quantity of the iodine solution equal to that required in the first titration is then placed in a flask, and 50 c.c. of the tin solution delivered into it, keeping the point of the pipette just below the surface; in this way, oxidation by air is completely avoided. A little starch is added and the titration finished with the iodine.

M. J. S.

**Electrolytic Estimation of Tin in Tin Ores.** By EDWARD D. CAMPBELL and E. C. CHAMPION (*J. Amer. Chem. Soc.*, 1898, 20, 687—690).—One gram of the finely ground ore is fused with 3 grams of sulphur and 3 grams of sodium carbonate in a covered porcelain crucible inserted in a larger one; this is then placed on a triangle and covered with a Hessian crucible, the bottom of which has been removed. After being heated for an hour to a full red heat, it is allowed to cool, the inner crucible is placed in a beaker with water to dissolve the soluble tin compound, and the insoluble portion is again fused with soda and sulphur and the two filtrates are united. Hydrochloric acid is now added until all the tin is precipitated, and the liquid is evaporated to about 75 c.c., mixed with 10 c.c. of hydrochloric acid, and fully oxidised by means of sodium peroxide. After filtering off from any sulphur, ammonia is added to the filtrate until the liquid becomes slightly turbid, and then 50 c.c. of a 10 per cent. solution of ammonium hydrogen oxalate is added, which will cause the solution to become clear. The liquid is now electrolysed during a night with a current N.D. 100 = 0.10 ampère with an E. M. F. of 4 volts. This will cause the metal to be completely precipitated as a pure white, firmly adhering coating upon the platinum dish, and after being washed first with warm water, and then with alcohol, it is dried and weighed. The dish, cleaned by dissolving off the tin with hydrochloric acid, is washed, dried, and weighed.

L. DE K.

**Estimation of Tin in Commercial Antimony.** By JOHN PATTINSON AND HUGH S. PATTINSON (*J. Soc. Chem. Ind.*, 1898, 17, 214—215).—In this process, advantage is taken of the very sparing solubility of antimony pentasulphate in cold strong sulphuric acid. About 6.5 grams of the pulverised metal is heated with 75 c.c. of sulphuric acid of sp. gr. = 1.83 until completely dissolved, which requires about 10 minutes, and then allowed to cool completely, when the greater part of the antimony sulphate crystallises out, whilst the tin, arsenic, copper, iron, and other impurities (except lead) remain in solution. The whole is thrown on an asbestos filter, the precipitate washed several times with sulphuric acid (sp. gr. = 1.83), and the filtrate diluted with 3 times its volume of water, cooled, nearly neutralised with ammonia, and treated with an excess of strongly yellow ammonium sulphide. All the metals except tin, arsenic, and antimony are precipitated, and are filtered off and washed with ammonium sulphide. The filtrate is then feebly acidified with dilute sulphuric acid and the sulphides of tin, arsenic, and antimony collected and washed. The precipitate is next boiled with a solution of bromine in strong hydro-

chloric acid, any sulphur which separates is oxidised by fuming nitric acid, and the united solutions are boiled until free from bromine. The greater part of the acid is now neutralised by ammonia, and the tin is separated from the other metals by Clarke's oxalic acid process, for which purpose oxalic acid is added to saturation and hydrogen sulphide passed through the hot solution; this throws down the arsenic and antimony, whilst the tin remains in solution. Finally, the filtrate is nearly neutralised with ammonia, an excess of ammonium sulphide added, and the stannic sulphide thrown down by acetic acid.

M. J. S.

**Assay of Telluride Ores.** By CHARLES H. FULTON (*J. Amer. Chem. Soc.*, 1898, 20, 586—597).—As telluride ores, when assayed for gold and silver, give less accurate results than other auriferous minerals, the author has made a laborious investigation into the cause of this, and has now greatly improved the process.

If the ore is very poor, 1 assay-ton of the powder is mixed with the same amount of dry soda, and half its amount of silica; 1—6 assay-tons of litharge, 10 grams of borax glass, and 2 grams of argol are added, and the whole well mixed and covered with salt. If traces of silver are likely to be present, an extra 0.02 gram of this metal is added, and also 4 iron nails to assist in desulphurising the ore. In dealing with rich ores, only one-fifth of an assay-ton is used with at least 2 assay-tons of litharge, 1 assay-ton of soda, and 1 gram of argol. The fire should be moderately hot, and the fusion should last from 40—50 minutes; the lead button obtained should weigh about 20—28 grams, and be, if possible, submitted at once to cupellation without previous scorification.

The traces of gold absorbed by the cupel may be disregarded, but the slag should always be powdered and remelted with another assay-ton of litharge and 2 grams of argol; the button formed is then also cupelled.

L. DE K.

**Examination of Otto of Roses.** By P. N. RAIKOW (*Chem. Zeit.*, 1898, 22, 149—150).—Dietze has proposed the following standard tests for the purity of otto of roses. (1) The sp. gr. at 15° should not exceed 0.870. (2) The solidification point should not be below 15—20°. (3) The rotatory power observed in a 100 mm. tube at 20° should not exceed  $-1^{\circ} 30'$ . (4) The saponification number should not exceed 9.5—10, and the relation between the acid and ether numbers not be higher than 7.

The author having tested the process with two samples of otto of roses of undoubted genuineness, states that the tests do not safeguard against an adulteration with oil of geranium.

L. DE K.

**Technical Analysis of Asphaltum and Asphalts.** By STEPHEN F. PECKHAM (*J. Soc. Chem. Ind.*, 1898, 17, 438—439).—For technical purposes, a more or less empirical examination is of greater value than a scientific analysis, and it is of primary importance to ascertain what proportion of the mineral is soluble in light petroleum, boiling oil of turpentine, and chloroform respectively. If the "organic matter not bitumen" is large in amount, its nature should be ascertained. The

amount and form of combination of the sulphur is next in importance, then the amount of the nitrogen and, lastly, that of the iron and aluminium. The solvents used should be carefully freed from water. Quantities of the mineral containing about 0.5 gram of bitumen are weighed into two 11 cm. extracted filters of known weight, placed in stop-cock funnels; the filters are filled with light petroleum which is allowed to run off slowly until the colour has perceptibly diminished, then the stop-cock is kept closed for 15—30 minutes after each addition of solvent and the last digestion should extend to 12 hours. The filters are dried at 66° and weighed. They are then exhausted with boiling oil of turpentine which is displaced by light petroleum before drying; the same filters are then exhausted with chloroform. They may next be extracted with 10 per cent. hydrochloric acid which removes calcium and magnesium carbonates and calcium sulphate; and lastly, they are deflagrated with sodium carbonate and potassium nitrate, and the sulphur present as pyrites, silica, iron, and aluminium are estimated in the fused mass. For total sulphur, a fresh portion of the mineral is deflagrated in the same way. Another portion is dissolved in benzene, the solution washed with dilute (10 per cent.) sulphuric acid, and the acid solution is treated with sodium nitrate when any nitrogenous basic oils present will be recognised by their odour. Another portion is exhausted with chloroform, and the residue extracted with ammonia for peat acids. Free sulphur will be found in the petroleum extract, organic aluminium compounds in the turpentine solution. Nitrogen may be determined by any method. The interpretation of the analytical results is reserved for a later communication. M. J. S.

**Estimation of Glycerol.** By FREDERIC WILLIAM RICHARDSON and ADOLF JAFFÉ (*J. Soc. Chem. Ind.*, 1898, 17, 330—333).—The only trustworthy methods for the estimation of glycerol are the dichromate and the acetin methods (Abstr., 1890, 425), and of these the dichromate process is the simpler and more satisfactory. The authors depart slightly from Hehner's instructions, relying on basic lead acetate for the removal of chlorides as well as of organic impurities, removing the excess of lead by dilute sulphuric acid and filtration before adding the dichromate. They recommend somewhat different proportions, namely, 20—25 c.c. of the glycerol solution, 25 c.c. of dichromate (Hehner's solution, of 74.86 grams per litre: 1 c.c. = 0.01 gram of glycerol), and 25 c.c. of concentrated sulphuric acid, and find that 20 minutes heating in the water-bath completes the reaction.

It is possible to estimate the glycerol in commercial samples by using a table of specific gravities, but it is necessary to determine the ash and to deduct certain constants from the specific gravity, in order to correct for the organic impurities usually present; these constants require to be varied for different percentages. M. J. S.

**Estimation of Phenols in Disinfectants in the Presence of Soap.** By WERNER SPALTEHOLZ (*Chem. Zeit.*, 1898, 22, 58).—The following process is recommended for testing compounds which contain the phenols in the free state; the sample is heated in an iron retort to 200°, and steam is passed through it until oily drops no longer come over with the distillate. The temperature during the distillation should

not exceed  $210^{\circ}$ , as otherwise any olein soap which may be present will undergo decomposition; rosin soap, however, may be heated without decomposition to  $220^{\circ}$ . The distillate is shaken with benzene to dissolve the phenols, and the benzene is then agitated with aqueous soda and the phenols precipitated from the alkaline solution by means of an acid. L. DE K.

**Estimation of Small Amounts of  $\alpha$ -Naphthol in Commercial  $\beta$ -Naphthol.** By JOHN PROCHÁZKA and H. N. HERMAN (*J. Soc. Chem. Ind.*, 1897, 16, 894—895).—The method is based on the fact that  $\alpha$ -naphthol combines with diazo-compounds more readily than  $\beta$ -naphthol does, and forms more soluble products. The diazo-compound employed is that of 1 : 4-naphthylaminesulphonic acid (naphthionic acid): 27.5 grams of (90 per cent.) sodium naphthionate is dissolved in 185 c.c. of water, 6.2 c.c. of concentrated sulphuric acid is diluted to 186 c.c. and slowly added with stirring, the mixture is cooled below  $5^{\circ}$ , and 7 grams of (98 per cent.) sodium nitrite in a 10 per cent. solution is slowly added; the paste obtained in this way is made up to 750 c.c. The  $\beta$ -naphthol solution is prepared as follows: 1.5 grams of  $\beta$ -naphthol, 200 grams of a 25 per cent. solution of sodium hydroxide, and 140 grams of a 10 per cent. solution of sodium carbonate are heated together until the  $\beta$ -naphthol is dissolved, and the solution is made up to 250 c.c. and cooled below  $5^{\circ}$  before use. To this  $\beta$ -naphthol solution, 37.5 c.c. of the diazo-solution (being  $\frac{1}{20}$  of the theoretical amount) is slowly added with stirring. If the  $\beta$ -naphthol solution is pure, the colour produced is entirely insoluble, but the presence of less than 10 per cent. of  $\alpha$ -naphthol is indicated by a peculiar bluish tint and the production of a coloured supernatant liquid. The amount of  $\alpha$ -naphthol can be very fairly estimated by dipping strips of filter paper into this liquid, and comparing the depth of tint with that produced by a solution of known composition. M. J. S.

**Paranitraniline Red.** By ADOLF LIEBMANN (*J. Soc. Chem. Ind.*, 1897, 16, 294—296).—Quantities of  $\alpha$ -naphthol greater than 0.1 per cent. present in the  $\beta$ -naphthol used for preparing paranitraniline red, are deleterious as regards the colour of the resulting dye.  $\beta$ -Naphthol can readily be freed from  $\alpha$ -naphthol by crystallising it from toluene, washing the crystals first with a mixture of toluene and light petroleum, then with the latter alone, steaming, and crystallising the steamed product several times from boiling water.

For determining the quantity of  $\alpha$ -naphthol in  $\beta$ -naphthol, the following process gives good results even when 0.01 per cent. only of the former is present; 0.144 gram of the  $\beta$ -naphthol is dissolved in 5 c.c. of absolute alcohol contained in a graduated test-tube, and the solution made up to 15 c.c. with pure toluene; 0.14 gram of paranitraniline dissolved in 9 c.c. of dilute hydrochloric acid is then cooled and diazotised with 1 c.c. of normal sodium nitrite, and 1 c.c. of the diazo-solution added to the tube containing the  $\beta$ -naphthol. Water is then added, the toluene solution separated and shaken with 5 c.c. of normal caustic soda, and the colour of the alkaline solution compared with that of the alkaline solution obtained in exactly the same way from  $\beta$ -naphthol containing a known quantity of  $\alpha$ -naphthol. The test is based on the fact that the hydroxyazo-derivative obtained from

$\alpha$ -naphthol and paranitraniline is soluble in alkalis, whereas the corresponding  $\beta$ -naphthol derivative is insoluble.

The following method of estimating metanitr-aniline in paranitr-aniline is available when more than 0.1 per cent. of the former is present. 0.25 gram of the paranitr-aniline is reduced to paraphenylenediamine by zinc dust and hydrochloric acid in a flask which permits gas to escape and yet does not allow air to enter; the colourless solution is then quickly filtered and diluted to 250 c.c. 0.25 gram of metanitr-aniline is reduced in the same way, and made up to 250 c.c. Ten c.c. of the paraphenylenediamine solution is then diluted to 50 c.c., and a drop or two of dilute sodium nitrite added; if the paranitr-aniline is pure, only a very slight change in colour occurs. If, however, metanitr-aniline is present, a light brown coloration (Bismarck brown) is produced; by comparing the latter with that obtained from a known quantity of the standard metaphenylenediamine solution, the amount of metanitr-aniline can be determined.

W. A. D.

**Estimation of Sugars as Osazones.** By CARL J. LINTNER and KROEBER (*Ann. Agron.*, 1898, 24, 448; from *Zeit. Brauwesen*, 1896, 153).—Twenty c.c. of the solution, which should not contain more than 1 per cent. of sugar, is heated for one hour and a half on a water bath with phenylhydrazine (1 gram) and 50 per cent. acetic acid (1 gram). In presence of dextrin, the heating must be prolonged to 2 hours. Boiling water (20 c.c.) is then added, and the osazone collected on a tared filter, dried at 110° for 3 hours, and weighed.

Saccharose, which is not completely inverted by acetic acid, is first inverted with hydrochloric acid; sodium acetate is then added, and the process continued as described.

The method is suitable for dextrose, levulose, and saccharose both alone and in presence of maltose and dextrans; the latter increase the weight of the osazone slightly.

N. H. J. M.

**Detection and Estimation of Glucose in Diabetic Urine.** By A. CARPENÉ (*L'Orosi*, 1897, 20, 157—160).—A quantity of urine containing not more than 0.2 gram of glucose is, if acid, neutralised with potash or, if alkaline, boiled to expel ammonia, mixed with a slight excess of lead acetate solution, filtered, and the precipitate on the filter washed with water. Five or six grams of glycerol are added to the filtrate and washings, and the liquid is then mixed with six times its volume of alcohol of 95—96°, filtered again if necessary, and about 10 c.c. of baryta water added. If glucose is present, a precipitate is produced, which may be collected, washed with alcohol of 95—96°, and converted into barium sulphate in the usual manner. Each decigram of the sulphate corresponds with 0.0772 gram of glucose. The test analyses given are very satisfactory. The glycerol in this process is added to prevent the precipitation of barium hydroxide by the alcohol. According to the author, the precipitate which glucose forms with baryta has the composition  $\text{BaC}_6\text{H}_{10}\text{O}_6$ , and not  $\text{Ba}(\text{C}_6\text{H}_{11}\text{O}_6)_2$ , as usually stated.

N. L.

**Clerget's Method of Estimating Saccharose.** By ARTHUR R. LING (*J. Soc. Chem. Ind.*, 1898, 17, 110—111).—The author gives

results confirmatory of Herzfeld's well-known formula,  $S = \frac{100K}{142.66 - 0.5t}$ , which is used when  $K$  stands for the difference between the readings of the Soleil-Ventzke-Scheibler polariscope, before and after the inversion of 26.048 grams of saccharose per 100 c.c. It is customary to make the solution after inversion of only half this strength, and to multiply the observed reading,  $i$ , by 2 before deducting it from the original reading. If any quantity other than 13.024 grams of sugar is inverted and diluted to 100 c.c., the formula becomes  $S = \frac{100K}{141.84 + 0.05i - 0.5t}$ .  
M. J. S.

**Modification of Clerget's Saccharimetric Process, applicable to After Products, and Molasses.** By ARTHUR R. LING and JULIAN L. BAKER (*J. Soc. Chem. Ind.*, 1898, 17, 111—114).—The authors recommend the use of invertase (compare O'Sullivan, *Trans.*, 1886, 58; 1891, 46) instead of hydrochloric acid for the inversion of saccharose, on the ground that, in highly impure substances, its hydrolytic action is more likely to be confined to saccharose than that of a mineral acid, and they show by experiments on pure sugar that identical results are obtained with the two inverting reagents. Satisfactory agreement is shown between duplicate determinations made by this process on various dark commercial products.

M. J. S.

**Estimation of Sugar in Chocolate.** By P. CARLES (*J. Pharm.*, 1898, [vi], 8, 245—257).—The optical method of determining sugar in chocolate is inaccurate, because it neglects to take into account the volume occupied in the solution by dissolved cocoa, and the rotation often caused by the latter. The values obtained by cupric reduction are also high, since, after inversion, substances, other than dextrose, which reduce Fehling's solution are often present. The following process, however, gives good results: 16.20 grams of the chocolate in thin shavings is heated with 80 c.c. of water during  $1\frac{1}{2}$  hours on the water-bath, 2—3 c.c. of a solution of basic lead acetate added, the mixture well shaken, and, after being diluted to 100 c.c. with water, filtered, and the amount of sugar determined by the saccharimeter. If  $N$  denotes the value thus obtained, the true percentage of sugar =  $0.919 N$ .

W. A. D.

**Estimation of Cellulose.** By GEORG LEBBIN (*Ann. Agron.*, 1898, 24, 352; from *Arch. Hyg.*, 1897, 28, 213).—The finely powdered substance (3 to 5 grams) is heated to boiling with 100 c.c. of water, for half an hour, to gelatinise the starch; 20 per cent. hydrogen peroxide (50 c.c.) is then added, and the boiling continued for 20 minutes, during which time 5 per cent. ammonia (15 c.c.) is added, 1 c.c. at a time. The mixture is then boiled for 20 minutes longer, filtered through a tared filter, the precipitate washed with boiling water, dried, and weighed; the weight of the ash is afterwards deducted. In some cases, the nitrogen is determined and the corresponding amount of protein also deducted. Concordant results, obtained with rye and wheat bran and with wheat grain, are given.



Filter paper treated with hydrogen peroxide and ammonia lost 2.72 to 5.65 per cent.

N. H. J. M.

**Estimation of Crude Fibre in Fodders and Foods.** By JOSEF KÖNIG (*Bied. Centr.*, 1898, 27, 706—711; from *Zeits. Unters. Nahrungs. u. Genussmittel*, 1898, 3).—The air-dried substance (3 grams), contained in a dry 500 c.c. porcelain dish, is stirred with nearly 200 c.c. of glycerol (sp. gr.=1.230) containing 30 c.c. of strong sulphuric acid per litre, the rest of the 200 c.c. being used to rinse the glass rod, when done with, into the dish; the dish is then placed in an autoclave and heated for an hour at 137° (3 atmospheres pressure). When cooled to 80—100°, the contents of the dish are diluted with 200—250 c.c. of boiling water, and at once filtered through asbestos; and as soon as the whole of the residue is on the filter, it is washed successively with 300—400 c.c. of boiling water, about 50 c.c. of alcohol (about 93 per cent.), and a warmed mixture of ether and alcohol, until the filtrate is colourless. The filter is dried until the weight is constant, weighed, ignited, and again weighed; the difference between the two weights is the amount of crude fibre free from ash. Gooch crucibles of 90 c.c. capacity and 35 mm. in diameter at the bottom were employed.

An alternative method, not involving the use of an autoclave, is also given. The substance is boiled with glycerol and sulphuric acid (the quantities are as given above) in a reflux apparatus for 1 hour; when the temperature reaches 120—130°, the contents generally froth, and the flask has to be shaken a few times. The process is afterwards completed as already described.

By the above method, the pentosans are removed either completely or nearly completely (to 6.62 per cent.). Leguminous fodders seem to be freed from pentosans with greater difficulty than gramineous fodders. The method is simpler, as well as more efficacious, than the older ones.

N. H. J. M.

**Separation and Estimation of Acids of the Saturated Fatty Series.** By SIGMUND HOLZMANN (*Arch. Pharm.*, 1898, 236, 409—441).—The author has prepared and studied the properties of the barium salts of the following acids: formic, acetic, propionic, butyric, isobutyric, isovaleric, hexoic, octoic, decoic, lauric, myristic, palmitic, stearic, and cerotic.

Experiments on the separation of the volatile acids are described, based on the supposition that, if a mixture of the alkali salts of several fatty acids be partially acidified with sulphuric acid and distilled, the acid of highest molecular weight passes over first, and on further acidification, the next lower acid, &c. (compare Wechsler, *Abstr.*, 1894, i, 12, and Crossley, *Trans.*, 1897, 580). Formic and acetic acids cannot be separated in this way, but with the higher members a partial separation is possible.

The solubility of the alkali salts of the volatile fatty acids in methylic and ethylic alcohols increases with the molecular weight, whereas amylic alcohol dissolves more sodium propionate than sodium butyrate. The salts of the lower members are not readily soluble in acetone, whereas sodium isovalerate is very soluble, and on cooling

the solution no milkiness is caused, but a separation of long, glistening, prismatic needles; by this means, isovaleric can be separated from propionic, butyric, or hexoic acid.

Ethyl palmitate, prepared by heating the acid with a 3 per cent. solution of hydrogen chloride in alcohol (yield 80 per cent. of theory) melts at  $24^{\circ}$  and boils at  $184.5\text{--}185.5^{\circ}$  at 10 mm. Ethyl stearate, produced in a similar manner (yield, the same), melts at  $33.5^{\circ}$  and boils at  $199\text{--}201^{\circ}$  at 10 mm. The melting and boiling points of mixtures of these two ethyl salts are given.

A. W. C.

### Sulphuric Acid as a Reagent in the Analysis of Fatty Acids

By ERNST TWITCHELL (*J. Soc. Chem. Ind.*, 1897, 16, 1002—1004).—The saturated fatty acids (palmitic, stearic, &c.) dissolve in, but are not sulphonated by, concentrated sulphuric acid, even at  $100^{\circ}$ ; on the other hand, oleic acid seems to be quantitatively sulphonated by acid of even 85 per cent., the sulphonated acid thus produced,  $C_{15}H_{31}\cdot CH_2\cdot CH(SO_4H)\cdot COOH$ , being practically insoluble in light petroleum, whilst the unattacked fatty acids can be dissolved out by petroleum, if acid not stronger than 85 per cent. has been employed. From 95 per cent. sulphuric acid, petroleum fails to dissolve out stearic and palmitic acids. For the examination of a mixture of saturated and unsaturated fatty acids, about 1 gram is solidified in a thin layer on the bottom of a stoppered conical flask, about 3 c.c. of 85 per cent. sulphuric acid is added, and the flask slightly warmed; as soon as a clear solution has been obtained, the flask is quickly cooled, 50 c.c. of light petroleum is added, the stopper inserted, and the flask violently shaken. The petroleum extract is then decanted, the flask twice rinsed with 10 c.c. of petroleum, and the united extracts washed with water and evaporated.

Lard yielded 42.3 per cent., two samples of cotton-seed oil 32.6 and 23.9 per cent. respectively, of saturated acids, having melting points of  $53\text{--}53.5^{\circ}$ .

M. J. S.

**Estimation of Tartaric Acid.** By JOHN MOSZCZENSKI (*J. Soc. Chem. Ind.*, 1898, 17, 215—216).—Goldenberg's "acid method," which, at the present time, is almost exclusively employed, does not provide for the separation of iron, aluminium, or the pectinic substances which are present in argols and lees, and which probably interfere greatly with the final titration. The following method excludes these substances, and is shorter than Goldenberg's. Five grams of the finely pulverised substance is treated with 26 c.c. of 13 per cent. sulphuric acid; this provides a sufficient excess of sulphuric acid for all ordinary materials, a large excess should be avoided. After stirring for a few minutes, the mixture is made up to 250 c.c. with alcohol of at least 90 per cent., well shaken, immediately thrown on a ribbed filter, and 200 c.c. of the filtrate measured into a basin; any long delay at this stage is objectionable, as there is a risk of ethyl tartrate being formed. An alcoholic solution of potassium acetate is now added as long as it produces a precipitate of potassium hydrogen tartrate; also 5 c.c. of strong potassium chloride solution. After 6 hours, the precipitate is col-

lected on a filter, washed with strong alcohol, and titrated as usual. A correction of 1.2 c.c. should be made for the bulk of the insoluble matter in the 250 c.c. flask, and 0.320 (? gram or per cent.) of tartaric acid should be added to the result to compensate for the solubility of potassium hydrogen tartrate in alcohol. The method is interfered with by the presence of potassium oxalate, as also is the case with Goldenberg's; phosphoric acid also raises the results, apparently to the extent of 1 molecule of tartaric acid for 1 molecule of  $P_2O_5$ .

M. J. S.

**Estimation of Potassium Hydrogen Tartrate in Wines.** By LOUIS MAGNIER DE LA SOURCE (*Chem. Centr.*, 1898, i, 149; from *Rev. Intern. Falsific.*, 10, 195—196).—First method.—Ten c.c. of the wine is evaporated over sulphuric acid to dryness, and meanwhile a solution is made by dissolving 1 gram of potassium hydrogen tartrate in 100 c.c. of water containing 10—12 c.c. of alcohol, and adding an excess of pure potassium sulphate; 10 c.c. of the filtrate is then added to the wine residue, so as to dissolve all matters except the cream of tartar and any potassium sulphate which may be present. After washing the insoluble matter with the same liquid, the residue is dissolved in hot water and titrated with standard baryta water.

Second method.—One hundred c.c. of wine is mixed with 1.5 gram of potassium sulphate, and evaporated down to 15 c.c.; after the lapse of 48 hours, the crystals are collected, washed with the alcoholic liquid already described, and finally titrated with baryta.

L. DE K.

**Analysis of Raw Materials containing Tartaric Acid.** By JOH. SCHÄFER (*Chem. Zeit.*, 1898, 22, 255—256; 269; and 404—405).—The first paper deals with the estimation of tartaric acid in argols, &c. To obtain correct results, Goldenberg's method, slightly modified, should be used. The original process, which is all but universally adopted, consists in heating the sample with dilute hydrochloric acid, neutralising the filtrate with excess of potassium carbonate, evaporating to a small bulk, adding acetic acid and alcohol, and finally titrating the potassium hydrogen tartrate with standard alkali. The author recommends first extracting any fatty matter by means of a mixture of alcohol and ether; after adding the acetic acid and alcohol, the mixture should not be allowed to stand overnight, but should be at once filtered. In titrating, feebly red litmus paper should be used as indicator.

The second paper is a reply to Eckstein's criticism (following abstract).

L. DE K.

**Analysis of Raw Materials containing Tartaric Acid.** By F. ECKSTEIN (*Chem. Zeit.*, 1898, 22, 351—352).—This is a criticism on Schäfer's article (preceding abstract). The chief point of interest is the author's condemnation of the use of red litmus paper. Violet litmus paper or azolithmin paper should be used when titrating the precipitated potassium hydrogen tartrate with standard soda. The rest of the paper is not adapted for abstraction.

L. DE K.

**Test for Uric Acid, and its Volumetric Estimation.** By TORQUATO GIGLI (*Chem. Zeit.*, 1898, 22, 330—331).—The paper is a preliminary communication on a new test for, and a volumetric estimation of, uric acid; 10 c.c. of the urine, or a solution of uric acid containing about the same quantity of the acid as occurs in urine, is mixed with 10 c.c. of a 7.5 per cent. solution of ammonium molybdate, and then with 10 c.c. of normal sulphuric acid. After a few minutes, 10 c.c. of normal soda is added, which causes the precipitate to redissolve; in the presence of uric acid, a bluish liquid is obtained. N/100 solution of potassium permanganate is now added, 1 c.c. at a time, until the liquid, which first becomes green and then yellow, changes to a reddish-yellow. This is the end reaction, and if the permanganate has been checked in the same manner with a known quantity of pure uric acid, the amount in the sample is readily calculated.

The author admits that urine probably contains matters which also reduce molybdic acid, and thus count as uric acid; the chief constituent of urine, the urea, does not, however, reduce the reagent.

L. DE K.

**Estimation of the Iodine Number.** By C. ASCHMAN (*Chem. Zeit.*, 1898, 22, 59; 71—72).—This is a modification of Hübl's process, the fats being measured instead of weighed, and a solution of iodine chloride used instead of the mercurial solution; 30 grams of potassium iodide is dissolved in 100 c.c. of water contained in a flask furnished with a side tube, which serves to carry off the excess of chlorine. Washed chlorine is now passed into the solution until the liberated iodine has redissolved, forming a dark yellow liquid. After being left for 6 hours in a cold place, potassium iodate and iodic acid separate. The clear liquid is then poured off, the crystals are washed four times with water, and the whole is made up to one litre. The solution is further diluted to such an extent that 10 c.c. of it, on adding 10 c.c. of a 20 per cent. solution of potassium iodide, liberates as much iodine as will correspond with 40 c.c. of N/10 sodium thiosulphate. The solution will keep unaltered for a year.

The fatty solution is made by measuring exactly 10 c.c. of the oil at 15°, or 10 c.c. of a melted fat at 50°, and dissolving this in exactly 10 c.c. of chloroform. Of this solution, 0.4 c.c. is carefully measured into a 250 c.c. flask, and after adding 10 c.c. of chloroform, 20 c.c. of the iodine chloride is introduced, the mixture is well shaken, and left for 24 hours in the dark with occasional shaking, when it is titrated with thiosulphate in the usual way, after adding 10 c.c. of 20 per cent. solution of potassium iodide.

A list of test results is given, the iodine figures being decidedly lower than those obtained by the original Hübl method. It is claimed, however, that they are more trustworthy and concordant. L. DE K.

**Detection of Sesame Oil in Butter or Margarines.** By PAUL SOLTSIEN (*Chem. Centr.*, 1898, i, 224; from *Pharm. Zeit.*, 1897, 42, 837; 846).—In applying the furfuraldehyde test to butter or margarine, care should be taken to use a hydrochloric acid of sp. gr. = 1.125, as the stronger acid of sp. gr. = 1.19 causes a distinct red coloration with furfuraldehyde alone, and also with turmeric, which is often used to

colour butters. Fats containing sesame oil give a permanent, fine red colour when heated on a water bath with stannous chloride; the colour is not discharged by moderately diluting with water. Turmeric also gives a reddish coloration with strong hydrochloric acid or stannous chloride, but the colour is not stable and disappears on adding water. L. DE K.

**Detection of Rape Oil.** By A. PALAS (*L'Orosi*, 1897, 20, 49—50).—Thirty cubic centimetres of a 0.1 per cent. solution of rosaniline are mixed with 20 c.c. of sodium hydrogen sulphite solution of 34°, 200 c.c. of water, and 5 c.c. of sulphuric acid of 65°. The reagent thus obtained, which should be perfectly colourless, is agitated in the cold with an equal volume of the oil to be tested, when a rose tint is developed if rape oil is present. Two per cent. of rape oil can be detected in olive oil by this means. The reaction is not given by other oils, neither is it given by the fatty acids of rape oil itself.

N. L.

**Apparatus for the Rapid Estimation of Fat in Soap, and of Hehner's Number.** By GIOVANNI POSSETTO (*L'Orosi*, 1897, 20, 73—76).—The apparatus consists of a flask of about 200 c.c. capacity, into the ground neck of which is fitted a glass tube graduated from 0 to 40 c.c. and closed at the top with a stopper. In order to determine the fatty acids in soap, about 1 gram of the sample is introduced into the flask and dissolved in hot water. The solution is then cooled, acidified with dilute sulphuric acid, the graduated tube inserted into the neck of the flask, and sufficient water added to bring the level of the liquid to the zero mark or thereabouts. Ether is now added, and the contents of the apparatus well mixed and allowed to settle; the volume of the ethereal layer is then read, and an aliquot part of it is pipetted off and evaporated, the residue being afterwards dried and weighed. For the determination of Hehner's number (percentage of insoluble fatty acids), 1—1.5 grams of the fat or oil is placed in the flask and dissolved in alcoholic potash, the alcohol being subsequently expelled by evaporation and the residual soap treated as above described.

The apparatus is also adapted for the estimation of the amount of oil in paints, and for other purposes.

N. L.

**Use of Lead Dioxide as a means of Clarifying Urine for Analysis.** By A. LOUBIOU (*J. Pharm.*, 1898, [vi], 8, 270—272; from *Bull. Soc. Pharm. Bordeaux*, July, 1898).—Turbid or fermented urine can be readily clarified by the following method; to 10 c.c. of it caustic soda is added until the solution becomes alkaline to phenolphthalein, 1.0—1.5 grams of lead dioxide is then added, and the mixture well shaken during a minute, and filtered. In the clear solution thus obtained, the albumin can be determined by Tanret's reagent; experiment shows that no albumin is removed by the lead dioxide during clarification. The process described is especially useful in the case of turbid biliary urine which cannot be obtained clear by other methods.

W. A. D.

**Modification of Mörner and Sjöquist's Method of Estimating Urea.** By HENRI MOREIGNE (*J. Pharm.*, 1898, [vi], 8, 193—197. Compare Abstr., 1891, 758 and 1561).—The process named

is more rapidly carried out by determining the nitrogen of the urea by means of sodium hypobromite, instead of by Kjeldahl's method, as originally recommended. After the process has been carried out as usual until the addition of magnesia, the solution is evaporated to 8 or 10 c.c., a little distilled water added, and the solution decanted from the magnesia; the latter is washed by decantation, and the washings added to the solution of urea, which is diluted to 50 c.c., and the urea present in 10 c.c., determined by the hypobromite method.

The above method gives lower results with urine than are obtained on purifying the latter by basic lead acetate, before estimating the urea; the difference is due to the ammonium salts not being removed in the latter process. W. A. D.

**Estimation of Urea in Urine by means of Sodium Hypobromite.** By HENRI MOREIGNE (*J. Pharm.*, 1898, [vi], 8, 197—200, and 241—245).—The results obtained by the ordinary method, using basic lead acetate to purify the urine, are too high, owing probably to the incomplete removal of ammonium salts (compare preceding abstract) and small quantities of guanine and creatinine. All the substances present in urine, including ammonium salts, which are capable of yielding nitrogen when acted on by sodium hypobromite, are, however, completely precipitated on adding phosphotungstic acid. It is important that the latter should be prepared as follows: 20 grams of sodium tungstate and 2.34 grams of crystallised phosphoric acid are boiled with 100 c.c. of water during 20 minutes, the solution slightly acidified with hydrochloric acid, and, after standing, filtered. To 10 c.c. of the urine, a small quantity of water is added, together with 4 c.c. of hydrochloric acid, and the amount of phosphotungstic acid (15—20 c.c.) necessary for accurate precipitation, and the whole diluted to 50 c.c.; after standing 24 hours, the solution is filtered, and 25 c.c. of the filtrate, rendered slightly alkaline by caustic soda, diluted to 50 c.c. The urea is estimated in 10 c.c. of the solution thus obtained by the hypobromite method.

In the case of certain pathological urines, it is advisable to subject the latter to a preliminary precipitation with basic lead acetate. After adding this and diluting the solution to a known volume, it is left for some time, filtered, and the lead precipitated in an aliquot portion by dilute sulphuric acid; any excess of the latter is neutralised with caustic soda, the solution acidified with hydrochloric acid, and the lead sulphate allowed to subside. One-half of the total volume is then filtered, precipitated with phosphotungstic acid, and the urea determined as above described. W. A. D.

**Relation between the Total Nitrogen of Urine and the Nitrogen Present as Urea.** By HENRI MOREIGNE (*J. Pharm.*, 1898, [vi], 8, 293—302).—Although the method of determining the total nitrogen of urine by Kjeldahl's process, generally adopted, is satisfactory, the methods for determining the nitrogen of the urea are by no means accurate (compare preceding abstract). If, for example, the solution to which sodium hypobromite is added, in the hypobromite method, contains more than 0.5 gram of urea in 100 c.c., an error as

great as 2·5—3 per cent. may arise ; the composition of the solution of hypobromite also exercises great influence on the volume of nitrogen obtained. In the author's opinion, little value can be attached to the ratio of total nitrogen of urine to urea nitrogen determined by other investigators.

W. A. D.

#### Volumetric Estimation of Alkaloids as Higher Periodides.

By ALBERT B. PRESCOTT and HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1898, 20, 706—728). See this vol., i, 89.

**Volumetric Method for the Estimation of the Total Alkaloids in "Cortex chinæ succirubr."** By H. EKROOS (*Arch. Pharm.*, 1898, 236, 328—334).—The finely powdered bark is extracted with a mixture of chloroform, ether, and aqueous soda for 3 hours, and a certain portion of the clear ethereal solution is then shaken with normal sulphuric acid, the excess of acid being titrated back with decinormal caustic potash solution, using a freshly prepared alcoholic solution of hæmatoxylin as indicator. The end of the reaction is denoted by a pale yellow colour, which, on vigorous shaking, changes to a bluish-violet.

The method can also be used for the analysis of quinine extracts.

A. W. C.

**Indigo Testing by Permanganate.** By J. GROSSMANN (*J. Soc. Chem. Ind.*, 1897, 16, 974—975).—It has been stated by Rawson (*J. Soc. Chem. Ind.*, 1885, 489) that, by direct titration with permanganate after sulphonation, a fairly approximate idea of the value of a sample of indigo can be formed ; the author shows, however, that, although this may be true as regards high class indigos (Bengal, Java), the method, when applied to low class samples (Kurpahs, Oudes), gives very variable results, which, in some cases, may err to the extent of 34 per cent. Results sufficiently trustworthy for practical purposes are, however, obtained if the sulphindigotic acid is precipitated by sodium chloride, and after washing is dissolved in dilute sulphuric acid and titrated. The instructions given by Rawson (not here reproduced) must be exactly followed, and they should be combined with the author's dye test, which is not described in this place.

M. J. S.

**Indigotin and Nitrobenzene.** By B. WILLIAM GERLAND (*J. Soc. Chem. Ind.*, 1897, 16, 108—109. Compare Abstr., 1898, ii, 102).—Carefully purified cold nitrobenzene dissolves indigotin very slowly ; on warming, however, a blue solution is obtained, which becomes tinged with red at 65°, and pure blood-red at 95°. On cooling, the solution remains red during several hours, but if a glass rod is introduced immediately becomes blue. Owing to the tendency to supersaturation which nitrobenzene solutions of indigotin exhibit, the solubility of the latter at the boiling point of the solvent could not be accurately determined ; the numbers vary from 0·5—1 gram in 100 c.c.

After indigotin has separated from its nitrobenzene solution, 25 c.c. of the filtrate contains only 0·000225 gram of indigotin ; in the author's process of determining indigotin (*loc. cit.*), this amount is quite negligible. The indigotin crystals, before weighing, should be

extracted on the filter with acid and alcohol, dried, washed with benzene, and digested with concentrated hydrochloric acid; after boiling with water and with aqueous sodium carbonate, the crystals are finally thoroughly washed with water, dried, and weighed. To determine indigotin in woollen and cotton fabrics, it is best to destroy the fibre by treatment with dilute sulphuric acid, and after filtering, washing, and drying to extract the residue with nitrobenzene.

The author has confirmed the accuracy of his method by comparing the results given by the latter with those obtained by the Müller-Bernthsen method; in addition, accurate results were obtained when known weights of indigotin were suitably adulterated, and then determined by the nitrobenzene method. W. A. D.

**Detection of Turmeric in Rhubarb Powder.** By ADAM JAWOROWSKI (*J. Pharm.*, 1898, [vi], 8, 303—304; from *Ann. Chim. Anal.*, 1898, 102).—If the powder contains turmeric, on agitating it with chloroform (10 c.c.) for several minutes, and filtering, a yellowish-brown solution is obtained with a greenish fluorescence; and on adding light petroleum (50 c.c.), a yellow, flocculent precipitate is formed, although the solution remains yellow and fluorescent. This is now divided into two portions; to the first, sulphuric acid (2—3 c.c.) is added, and to the second, a saturated solution of borax (1—1.5 c.c.). In presence of turmeric, the former becomes violet, whilst the acid layer, at first bright red, becomes successively reddish-brown and yellow; the borax solution becomes coloured violet, without, however, any colour-change taking place in the petroleum layer. W. A. D.

**Standard Methods for the Sampling and Analysis of Tanning Materials.** By HENRY R. PROCTER and J. GORDON PARKER (*J. Soc. Chem. Ind.*, 1898, 17, 6—10).—This communication makes public the resolutions on the above subject adopted by an International Conference of the Chemists connected with the leather industry, held in London on September 28—30, 1897. The "hide powder" method was adopted for the estimation of tannin. The resolutions came into force on January 1st, 1898, and all leather trades' chemists who are members of the Association have agreed to work by the Conference methods until these are altered at a future Conference. M. J. S.

**Chemical Method of Ascertaining whether Milk or Cream has been Heated to at least 80°.** By V. STORCH (*Bied. Centr.*, 1898, 27, 711—714; from 40<sup>de</sup> *Beret. kgl. Vet. Landbohøjskoles Lab. landökon. Fors. Copenhagen*, 1898, 1—16).—Not only mixed milk, but the milk of single cows during the whole period of lactation, shows a bluish-grey coloration when treated with a drop of dilute hydrogen peroxide and a few drops of a 2 per cent. solution of paraphenylenediamine. The action seems to be rather less in the case of cream and rather greater with butter milk, probably owing to the varying amount of fat globules present.

Whey produces a dark violet-brown colour. It is supposed that the blue coloration obtained with milk is the result of a special interaction of the casein and the diphenylenediamine.



Butter milk from sour cream gave the coloration only when the free acid was partly neutralised with lime water. Milk fat globules free from milk serum, and pure casein solutions, gave no coloration.

The "active substance" could not be obtained quite pure. It is especially abundant in the deposit which forms on the inner side of a centrifugal separator. When obtained as free as possible from proteids, the aqueous solution gives the same violet-brown coloration as is obtained with whey, but when added to boiled milk (which gives no coloration with hydrogen peroxide and paraphenylenediamine) the dark blue colour is at once obtained.

Milk which has been heated to 79–80° may still produce the blue coloration, provided that it is cooled as soon as that temperature is reached. Heating for 2 minutes at 75° is sufficient to destroy the "active substance" if the cooling is slow.

As regards the effect of acidity, it was found that, whilst with milk which required 17 c.c. of N/10 alkali to neutralise 100 c.c., the limit of temperature was 79°, butter milk which required 90 c.c. of alkali was rendered inactive by heating to 71°.

The reaction is not without importance in the case of Pasteurisation. It sometimes happens that the whole of the milk has not been heated to 79°. Milk heated to 82°, mixed with 10 per cent. of milk heated to 78°, showed the blue coloration distinctly. The presence of 1 per cent. of milk heated at 75° could also be detected. N. H. J. M.

**Gelatin in Chocolate.** By P. ONFROY (*J. Pharm.*, 1898, [vi], 8, 7–9).—In presence of 5 per cent. of gelatin, as much as 10 per cent. of water can be added to chocolate without altering the latter's appearance. When a considerable proportion of gelatin is present it can be detected by boiling the chocolate (5 grams) with water (50 c.c.), adding 5 c.c. of 10 per cent. solution of lead acetate, filtering and adding a few drops of a saturated solution of picric acid; the latter produces an immediate, light yellow, amorphous precipitate with solutions containing more than 0.01 per cent. of gelatin. When only a small quantity of gelatin is present in a chocolate, it is rendered insoluble by the tannin of the latter, and the following method has to be adopted for its detection. After removing the fat from 10 grams of the sample by means of ether, 100 c.c. of warm water is added, then 5–10 c.c. of a 10 per cent. solution of potassium carbonate, and 10 c.c. of 10 per cent. lead acetate; on filtering and carefully neutralising, a solution is obtained which can be tested for gelatin by the ordinary methods. W. A. D.

## General and Physical Chemistry.

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**Magnet-radiometer.** By NICOLAE TECLU (*J. pr. Chem.*, 1898, [ii], 58, 255—260. Compare Abstr., 1893, ii, 401).—The paper contains a detailed description and photograph of the “magnet-radiometer” designed by the author for use in the diaphanometer previously described by him (*loc. cit.*). The outer portion of the vane of a radiometer is coated with a very thin layer of iron, so that movements of the vane can be caused, not only by the action of light rays, but also by the approach of a magnet; when both forces are applied simultaneously, the position assumed by the vane will be a resultant of the two, and so can be applied to the measurement of the intensity of the light falling on the instrument. A. W. C.

**Yellow Light for the Polarimeter.** By FRANÇOIS DUPONT (*Bull. Soc. Chim.*, 1897, [iii], 17, 584).—A much more satisfactory yellow light for polarimetric observations is obtained when a mixture of sodium chloride and trisodium phosphate, in molecular proportions, is used in place of sodium chloride alone. J. J. S.

**Normal Elements.** By DOUGLAS MCINTOSH (*J. Physical Chem.*, 1898, 2, 185—193).—The object of the author in undertaking this research was to find a convenient standard having an E.M.F. of about 0.5 volt. A cell consisting of zinc, zinc chloride, lead chloride, and lead, as described by Baille and Féry, gives good results, and has an E.M.F. of 0.5 at 20° when the specific gravity of the zinc chloride is 1.23. The temperature coefficient is extremely low. A great many cells in which mercuric oxide was used as a depolariser were tried, but none of these were satisfactory, and the use of other oxides as depolarisers gave negative results. Cells of copper, copper sulphate, mercurous sulphate, and mercury were tried and gave excellent results. The copper sulphate and mercurous sulphate are each taken in the form of a paste. The E.M.F. of this cell decreases with rising temperature, and in the neighbourhood of 16.5° may be calculated by the formula  $E = 0.3613 + (16.5 - t)0.0006$  volt. Cells containing Pb, PbCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, Hg were also examined, and gave satisfactory results. The E.M.F. increases with the temperature, and may be calculated approximately between 15° and 21° by the formula  $E = 0.5382 + (t - 21)0.0006$ . H. C.

**Determination of Polarisation.** By KARL HEIM (*Zeit. Elektrochem.*, 1898, 4, 527).—In an electrolytic cell of resistance  $R$ , with insoluble anode, through which current  $C$  is passing with E.M.F.  $= E$ , we have  $E = p + CR$ , where  $p$  is the polarisation. If a thin sheet of metal be interposed between the electrodes so as to divide the cell completely, without sensibly affecting its resistance, and the current be maintained unchanged, we have  $E' = 2p + CR$ , or  $p = E' - E$ . In putting the method into practice, the main difficulty is encountered in arranging the cell so that the third electrode may be put in or taken

out easily, and in such a way that the current shall pass through it, and not round it. A rectangular ebonite cell is provided with platinum electrodes fitting into grooves in the walls 60 mm. apart. Between these, a third groove, 8 mm. deep and 0.25 mm. wide, receives the third electrode. This depth is sufficient to prevent undue leakage round the electrode with moderate conductivities and current densities. A greater depth would be better. About half an hour elapses before the polarisation becomes constant. The following are some of the results obtained.

Copper sulphate, 16 per cent. at 14.7—14.95°.

Current density... 0.03 0.06 0.12 0.2 0.3 amp./sq. dcm.

Polarisation ..... 1.591 1.628 1.668 1.695 1.717 volts.

Silver nitrate, about normal, at 15—15.5°

Current density... 0.015 0.03 0.06 0.12 0.2 0.4 amp./sq. dcm.

Polarisation ..... 0.888 0.897 0.903 0.908 0.926 0.935 volt.

T. E.

**Pulverisation of Metal Cathodes During Electrolysis with a Constant Current.** By GEORG BREDIG and FRITZ HABER (*Ber.*, 1898, 31, 2741—2752. Compare Abstr., 1898, ii, 364).—When a cathode consisting of a bright lead plate or wire conveying a current at 24—72 volts is brought into dilute sulphuric acid, a platinum anode being employed, a momentary pulverisation of the lead occurs, and a fine, metallic powder falls through the liquid. This takes place at isolated spots on the surface of the metal, bright indentations being left with rounded edges. A similar phenomenon takes place in alkaline solutions, but in this case is continuous and much more energetic. The metallic lead thrown down is peculiarly susceptible to chemical change, and can readily be converted into white lead by the simultaneous action of air and carbonic anhydride. The addition of small quantities of a chromate or chromium salt prevents the occurrence of the phenomenon. Mercury, tin, bismuth, thallium, arsenic, antimony, and Rose's metal all show the same phenomenon in alkaline solutions, whereas cadmium, zinc, copper, silver, aluminium, platinum, and palladium do not act in this way. In acid solution, on the other hand, only bismuth and Rose's metal behave in a similar manner to lead. The phenomenon is to be distinguished from the loosening of the surface which occurs with cathodes of platinum, palladium, and lead. In alkaline solution, it is probably preceded by the formation of an alloy of the metal of the cathode with the alkali metal present, which is then decomposed by the water. This is especially marked in the case of mercury, but no similar action can occur in acid solution.

A. H.

**Electrolytic Decomposition of Aqueous Solutions.** By L. GLASER (*Zeit. Elektrochem.*, 1898, 4, 355, 373, 397, and 424).—The author first repeats the experiments of Smale (Abstr., 1894, ii, 436) on the oxygen-hydrogen gas cell, and confirms his conclusion that the formation of water in this cell takes place in a reversible way at the E.M.F. of 1.08 volts. He then goes on to determine the E.M.F.'s required to separate the ions contained in various aqueous solutions from their electrical charges. The observations are made by applying any desired

E.M.F. from zero upwards to a pair of electrodes immersed in the solution under examination, and noting the current which is thereby caused to pass through the cell. When the E.M.F. is less than that required to produce continuous decomposition, a very small diffusion current is observed. When the decomposition point is reached, the current increases more or less suddenly, so that at each decomposition point a change in the direction of the curve connecting current and E.M.F. is observed. One of the electrodes is made of platinised platinum saturated with atmospheric oxygen, and is very large compared with the other; in this way, its polarisation is rendered practically constant and the changes of direction observed are due to separation of ions at the small electrode.

The small electrode being used as cathode, a decided increase of current is found at 1.08 volts with dilute sulphuric acid, and a much less decided change at the same E.M.F. with solutions of sodium or potassium hydroxide; the difference is due to the small number of hydrogen ions in the solutions of the bases. In all cases, a decomposition point is better marked the greater the quantity of the particular ion which is present.

When the small electrode was used as anode and the large oxygen electrode as cathode, an exceedingly well marked decomposition point was found at 0.59 volt with solutions of sodium or potassium hydroxides, and a much less marked decomposition point at 0.6 volt with dilute sulphuric acid.

The ion separated here is, therefore, hydroxyl. Measured in both cases with reference to the large oxygen electrode, 1.08 volts are therefore required for the continuous separation of hydrogen and 0.59 volt for that of hydroxyl. The sum of these quantities, 1.67 volts, is the frequently observed polarisation in the ordinary electrolysis of dilute aqueous solutions. That visible electrolysis can be produced with 1.08 volts is explained by assuming the separation of  $\bar{O}$  ions, the very minute amount of these ions present accounting for the slow course of the decomposition.

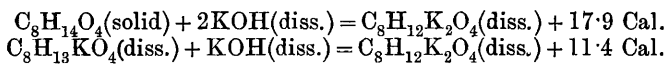
When a solution of potassium hydroxide is electrolysed, using the small electrode as cathode, two changes of direction are observed in the current-E.M.F. curve. The first, at 1.08 volts, corresponds with the separation of the hydrogen ions from their charges, whilst the second corresponds to the separation of potassium ions. The position of the second point varies with the concentration of the potash solutions, the following values being found: 10N, 1.32 volts; 4N, 1.38 volts; 1N, 1.4 volts;  $\frac{1}{2}$ N, 1.45 volts;  $\frac{1}{10}$ N, 1.46 volts. Similar results are obtained with other bases, the values being,

1	normal KOH	1.4 volts
1	NaOH	1.315 "
0.0002	Mg(OH) <sub>2</sub>	1.395 "
0.02	Ca(OH) <sub>2</sub>	1.33 "
0.22	Ba(OH) <sub>2</sub>	1.185 "
0.063	Sr(OH) <sub>2</sub>	1.20 "

From the latter measurements, it follows that the separation of hydrogen from aqueous solutions is only primary with very small

electromotive forces ; with any ordinary current, the greater part of it is due to secondary action. T. E.

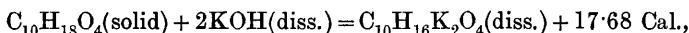
**Thermochemistry of Suberic Acid.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1897, [iii], 17, 745—746).—Suberic acid crystallises in brilliant, white scales melting at  $139.5^{\circ}$ ; one litre of water at  $17^{\circ}$  dissolves about 1.8 grams of the acid, the heat of dissolution being  $-5.45$  Cal. Normal potassium suberate becomes anhydrous at  $100^{\circ}$ , and dissolves in water with the development of  $+0.92$  Cal. Potassium hydrogen suberate is only very slightly soluble in cold water ; its heat of dissolution is  $-5.26$  Cal. at  $40^{\circ}$ . When a solution of this salt is concentrated on the water-bath, suberic acid first crystallises out, and then the acid salt, whilst the more soluble normal salt remains in solution. From the heats of neutralisation,



it is calculated that the heats of formation of normal potassium suberate and potassium hydrogen suberate are  $+44.76$  Cal. and  $+25.67$  Cal. respectively, all the substances concerned being in the solid state.

N. L.

**Thermochemistry of Sebacic Acid.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1897, [iii], 17, 746—747).—Sebacic acid crystallises in anhydrous, nacreous scales melting at  $129^{\circ}$ . One litre of water at  $16^{\circ}$  dissolves 0.55 gram of the acid, without sensible development of heat. Normal potassium sebate crystallises with one molecule of water, and dissolves in water with the absorption of  $-1.33$  Cal.; it does not lose water at  $100^{\circ}$ , nor when placed in a vacuum over sulphuric acid, but the anhydrous salt is obtained by heating at  $150^{\circ}$  in a current of dry hydrogen. Its heat of dissolution is  $+1.47$  Cal. From the heat of neutralisation,



it is calculated that the heat of formation of normal potassium sebate is  $43.99$  Cal., all the substances concerned being in the solid state.

Potassium and sodium hydrogen seabates are not sufficiently soluble in water to allow of thermochemical study by the usual methods.

N. L.

**Normal Dibasic Acids of the Oxalic Series.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1897, [iii], 17, 747—748).—The heats of formation of the anhydrous normal potassium salts of some acids of the oxalic series have been found to be as follows : oxalic acid,  $+58.97$  Cal.; malonic acid,  $+48.57$  Cal.; succinic acid,  $+46.40$  Cal.; glutaric acid,  $+44.23$  Cal.; suberic acid,  $+44.76$  Cal.; sebacic acid,  $+43.99$  Cal. From these results, it appears that, as the molecular weight of the acid and the distance between the two carboxyl groups increase, the heat of formation of the salt decreases, and ultimately approaches that of two molecules of potassium acetate ( $43.72$  Cal.). The influence of the carboxyl groups on each other decreases rapidly with the introduction of intermediary  $\text{CH}_2$ -groups, a fact which is in accordance with the formation of anhydrides from these acids, succinic anhy-

dride being easily obtained and glutaric anhydride with difficulty, whilst the higher members of the series seem to be incapable of existence. A similar relationship is observed in the production of lactones from acids of the lactic series. N. L.

**Acetaldoxime.** By HECTOR R. CARVETH (*J. Physical Chem.*, 1898, 2, 159—167).—The author has repeated Dunstan and Dymond's experiments on the freezing point of acetaldoxime (*Trans.*, 1892, 61, 471; 1894, 65, 206), and confirmed them in every detail. All the freezing point phenomena can be accounted for on the assumption of an equilibrium between two modifications in the liquid phase. Although the rate of change of the freezing point of acetaldoxime is a function of the temperature to which the substance is heated, the final equilibrium is independent of the temperature. Heating to  $114.5^{\circ}$  causes the freezing point to drop from  $47^{\circ}$  to  $13^{\circ}$ , and also if the crystals are kept long enough at  $20^{\circ}$  they will liquefy, and if the liquid is kept for about 10 days and then cooled, the freezing point will be found to be  $13^{\circ}$ . In other words, the equilibrium is not displaced by the temperature, and the relative amounts of these two modifications is not a function of the temperature. The liquefaction of the crystals is not accompanied by a measurable change of vapour pressure, and the author regards it as probable that two modifications exist in the vapour. Sunlight does not produce any visible effect. H. C.

**Determination of the Specific Gravity of Pulverulent Substances.** By GUSTAV J. W. BREMER (*Rec. Trav. Chim.*, 1898, 17, 263—269).—By the following method, more accurate results can be obtained than by using Kopp's volumometer, and small quantities only of the substance dealt with are necessary; the difficulty of removing air bubbles in the ordinary method, using a pycnometer, is also obviated. A flask ( $F$ ), having a capacity of from 3—15 c.c., is surrounded by cold water, and is connected to a three-way stop-cock ( $R$ ) fitted to the top of a manometer tube ( $a$ ) which is closed below by an ordinary tap,  $S$ , through which it communicates by india-rubber tubing with a pressure tube ( $C$ ),  $R$  enables the flask  $F$  to be in connection with the manometer tube alone or with both it and the air simultaneously. The pressure tube is filled with mercury; by raising  $C$ , the level of the mercury in  $a$  is brought to coincidence, under atmospheric pressure,  $H$ , with the upper edge ( $p$ ) of a window in a ring which slides on  $a$  near the top. By turning  $R$  through  $180^{\circ}$ , the connection between the flask and the air is broken, and the tube  $c$  is then lowered until the level of the mercury in  $a$  coincides with the upper edge ( $q$ ) of the window in a second ring placed near the bottom of  $a$ . The difference in level,  $h$ , of the mercury in the tubes  $a$  and  $c$  is measured by a cathetometer.

The observations described are then repeated after introducing a weighed amount,  $w$ , of the substance taken into the flask  $F$ . If  $h'$  denote the new difference of level in the tubes  $a$  and  $c$ , corresponding to the original  $h$ ;  $H'$  the atmospheric pressure during the latter part of the experiment,  $v$  the volume occupied by the mercury between the levels of the upper edges of the windows  $p$  and  $q$ , and  $a$  the required

volume of the powder, then  $x = v \left( \frac{H}{h} - \frac{H'}{h'} \right)$ . If, as is usual,  $H = H'$ ,  $x = vH \left( \frac{h' - h}{hh'} \right)$ ; and the required density  $d = \frac{whh'}{vH(h' - h)}$ . Since the accuracy of the method is a maximum when  $v = \sqrt{VV'}$ ,  $V$  denoting the volume of the flask  $F$  and of the tubes connecting it with the manometer, as far as the upper level of the window  $p$ , and  $V'$  the volume  $V - x$ , the ring  $p$  is moved, before carrying out the experiment, into such a position that  $v = \sqrt{VV'}$ , approximately. Care is taken throughout that the temperature of the flask  $F$  is kept constant.

W. A. D.

**Vapour Tension of Concentrated Hydrochloric Acid Solutions.** By F. B. ALLAN (*J. Physical Chem.*, 1898, 2, 120—124).—If the action of hydrogen chloride on water resulted only in the electrolytic dissociation of the hydrogen chloride, the relation between the undissociated molecules in a given volume of the solution and the pressure of the gas should be a constant. Vapour pressure measurements were made by forcing air through hydrogen chloride solutions, absorbing the vaporised gas in water in Liebig bulbs, and titrating with a potash solution. The vapour pressures of the solutions examined were found to be as follows.

% HCl.	Pressure in mm.	% HCl.	Pressure in mm.	% HCl.	Pressure in mm.
36.40	138.1	34.85	66.6	31.75	21.9
35.90	109.8	33.90	46.0	30.20	11.8
35.10	75.8	32.85	32.7	28.10	5.5

The above readings give a very regular curve. If the vapour tension is taken as proportional to the undissociated hydrogen chloride, the degree of dissociation in a 28.1 per cent. acid is 94.8. This is an impossible value for so concentrated a solution, and it is concluded, therefore, that electrolytic dissociation is not an adequate explanation of the fact that hydrochloric acid solutions do not obey Henry's law.

H. C.

**Naphthalene and Aqueous Acetone.** By HAMILTON P. CADY (*J. Physical Chem.*, 1898, 2, 168—170).—Mixtures were made of acetone and water, and naphthalene in excess added to each solution, and the temperatures determined at which a second liquid phase first appeared. The temperatures at which different solutions begin to separate into two layers in presence of solid naphthalene, and the compositions of these solutions, are as follows.

Acetone.	Water.	Naphthalene.	Temperature.
10.00	89.92	0.08	65.5°
19.91	80.00	0.09	55.3
29.92	69.67	0.41	45.0
40.81	58.22	0.97	38.0
48.67	48.68	2.65	32.2
57.43	36.64	5.93	28.5
60.43	25.75	13.82	28.2

The effect of a very small quantity of naphthalene on the consolute temperature is very marked.

H. C.

**Distribution of Mercuric Chloride between Toluene and Water.** By OLIVER W. BROWN (*J. Physical Chem.*, 1898, 2, 51—52).—According to Skinner (*Trans.*, 1892, 61, 342), a fairly constant distribution ratio is obtained when mercuric chloride is added to mixtures of ether and water. Experiments made by the author with toluene and water show that the ratio of the concentrations is not constant in this case, the concentrations in the water phase not increasing quite so rapidly as those in the toluene phase. This would mean, according to the Nernst theory, that there is a slight dissociation in the aqueous solution. H. C.

**Solubilities of some Sparingly Soluble Liquids in Water.** By W. HERZ (*Ber.*, 1898, 31, 2669—2672).—The author has determined the mutual solubility of a number of liquids and water, with the following results.

1000 c.c. of water	dissolve 4.20 c.c. of chloroform,	forming 1003.9 c.c. of solution.
" "	" 1.74 "	carbon bisulphide,
" "	" 3.41 "	forming 1002.08 "
" "	" 81.10 "	light petroleum (sp. gr. 0.6646) "
" "	" 0.82 "	ether "
" "	" 32.84 "	benzene "
" "	" 34.81 "	amylic alcohol "
" "	" "	aniline "
" chloroform	dissolve 1.52 "	water "
" carbon bisulphide	dissolve 9.61 "	" "
" light petroleum	dissolve 3.35 "	" "
" ether	" 29.30 "	" "
" benzene	" 2.11 "	" "
" amylic alcohol	dissolve 22.14 "	" "
" aniline	" 52.22 "	" "

A. H.

**Indicators.** By JOHN WADDELL (*J. Physical Chem.*, 1898, 2, 171—184).—According to the dissociation theory, an indicator must be a weak base or a weak acid in which one of the ions has a different colour from that of the undissociated substance. Under these circumstances, the presence in the solution of a liquid in which the indicator dissociates to a less extent than in water should cause the colour due to the ion to disappear more or less. Nine indicators were, therefore, taken, and tested in presence of alcohol, acetone, ether, benzene, and chloroform. The results obtained were in keeping with the dissociation theory. In alcohol and acetone, the colour of the ion is often perceptible, but this disappears when any one of the other organic solvents is added. It is often possible to predict the acid or basic properties of an indicator from the colour changes on the addition of organic solvents. Methyl-orange and lacmoid act as weak bases; fluorescein, phenacetolin, and probably corallin are both basic and acid. More satisfactory results were obtained with ammonia and acetic acid than with caustic potash and hydrochloric acid. This the author



regards as due to the dissociation, to some extent, of salts of weak acids and weak bases into the free acid and free base in organic solvents.

H. C.

**Fractional Crystallisation.** By CHARLES A. SOCH (*J. Physical Chem.*, 1898, 2, 43—50).—Solubility determinations of the pairs of salts, potassium chloride and potassium nitrate, potassium chloride and sodium chloride, potassium nitrate and sodium chloride, and sodium nitrate and sodium chloride were made at 25° and at 80° in pure water, and at 25° in 40 per cent. aqueous alcohol. The results are given in the following table, the concentrations being in grams of salt per hundred grams of solvent.

	Aqueous alcohol at 25°.	Water at 25°.	Water at 80°.
{ KCl.....	10·06	34·12	40·20
{ KNO <sub>3</sub> .....	5·29	22·58	117·5
Ratio .....	1·90	1·51	0·361
{ NaNO <sub>3</sub> .....	22·78	43·66	121·6
{ NaCl.....	10·17	26·58	17·62
Ratio .....	2·24	1·64	6·90
{ KNO <sub>3</sub> .....	13·74	41·14	168·8
{ NaCl.....	15·78	38·53	39·81
Ratio.....	0·87	1·07	4·14
{ NaCl.....	12·28	29·05	26·5
{ KCl.....	5·87	17·1	31·0
Ratio.....	2·09	1·70	0·855

From the above, it will be seen that the displacement of the equilibrium by the addition of alcohol is in no case as large as the change produced by difference of temperature. A short theoretical treatment of the subject of fractional crystallisation by Bancroft is added.

H. C.

**Absorption.** By JACOBUS M. VAN BEMMELN (*Zeit. anorg. Chem.*, 1898, 18, 98—146).—The continuation of the author's research is in accordance with the previous results (*Abstr.*, 1897, ii, 137, and this vol., ii, 12). The elimination of water from the hydrogel, up to a certain point, takes place without the formation of water-free interstices, the decrease in volume corresponding with the amount of water evaporated. The greater part of the water evaporates at 15°, with a rapidity little less than that of water itself. As the remaining water evaporates at a steadily increasing vapour pressure, the colloid gradually assumes a solid, glassy condition. The point at which the elimination of water ceases, under a given vapour pressure, varies with the method of formation and age of the colloid, the rapidity of the evaporation, and temperature. In the reabsorption of water by a partially dried colloid, a higher vapour pressure is necessary in order to obtain the same amount of water in the colloid as was present before drying. The absorbing properties of the colloid are decreased by formation in a concentrated silica solution, by prolonged drying, and by time. At a red heat, the absorbing properties are lost.

E. C. R.

**General Problem of Chemical Statics.** By PIERRE DUHEM (*J. Physical Chem.*, 1898, 2, 1—42 and 91—115).—A mathematical paper not suitable for abstracting. H. C.

**Combination of Gases.** By H. HÉLIER (*Ann. Phys. Chim.*, 1897, [vii], 10, 521—556).—The author describes the furnace, pyrometer, and gas apparatus employed by him in studying the combination of gaseous mixtures at definite temperatures. Experiments, made on a mixture of hydrogen and oxygen containing the gases in combining proportions, show that at any given temperature there is a certain limit of combination, and that, after a certain time, continued heating produces no further interaction. This limit is reached in a relatively short time; in the case of oxygen and hydrogen heated to 300°, the time required is 17 seconds. The amount of water produced varies with the temperature, at 180° it is only 0.04 per cent., at 825° it is 96.1 per cent., and combination takes place explosively at 853° (Abstr., 1896, i, 416). This temperature of explosion is 300° above that indicated by Mallard and Le Chatelier. Van't Hoff defined the temperature of explosion as that at which the initial loss of heat due to conduction, &c., is equal to the heat produced in the same time by the chemical reaction. It may, therefore, be raised considerably by increasing the initial loss of heat of the gaseous mixture.

Experiments made on the above mixture in the presence of nitrogen, show that the inert gas hinders the combination; at 491°, the decrease produced by the addition of 1½ volumes of nitrogen is 17.4 per cent. Half the quantity of nitrogen produces approximately half this diminution. Excess of oxygen or hydrogen increases the amount of combination, but, volume for volume, excess of oxygen produces greater effect than excess of hydrogen.

A mixture of carbonic oxide and oxygen, in combining proportions, begins to react at 195°, the amount of combination increases slowly up to 500°, and more rapidly up to 855°, when it amounts to 65 per cent.

The presence of nitrogen diminishes the amount of combination. The inert gas also decreases the velocity of combination; with the normal mixture of carbonic oxide and oxygen at 549°, the limit is reached in 30 seconds; in the presence of 1½ volumes of nitrogen, the limit is attained only after 70 seconds.

An excess of oxygen increases the percentage of combination, excess of carbonic oxide, on the contrary, diminishes the amount of carbonic anhydride produced. The walls of the vessels in which gaseous combination occurs have a marked influence on the results (compare Abstr., 1897, ii, 437, 486, and 548).

The combination of hydrogen and oxygen is always complete when the normal mixture is heated for 5 hours in tubes of potash glass, and the water produced is strongly alkaline; in tubes of lead glass, the combination, carried out under similar conditions, is far less complete, and some of the hydrogen is used up in reducing the lead silicate present. In new silvered tubes, the combination is complete, but on repeating the experiment the amount of water formed, although variable, never indicates complete combination.

The presence of water vapour decreases the amount of combination.

This cannot be due to the fact that there is any tendency towards a reverse action, since the effect is well marked at temperatures far below that at which steam dissociates. The combination of gases at any temperature attains a limit, not because the reaction is reversible, but because the presence of the products of combination appears to hinder the completion of the reaction. G. T. M.

**Report of the Committee of the German Chemical Society on Atomic Weights.** By the Members of the Committee: HANS LANDOLT, WILHELM OSTWALD, and KARL SEUBERT (*Ber.*, 1898, 31, 2761—2768).—This report is issued by the committee appointed by the German Chemical Society on December 1, 1897, to consider the question of atomic weights, and to draw up a table of the most probable values of these constants for general use. The members of the committee were unanimous in adopting the two following conclusions.

I. The atomic weight of oxygen shall be taken as the standard, and assigned the value 16·000; the atomic weights of the other elements to be then calculated from their, directly or indirectly determined, combining proportions with oxygen.

II. The numbers which may at present be taken for practical purposes to represent the probable atomic weights of the elements are as follows.

Aluminium .....	Al	27·1	Neodymium (?)...	Nd	144
Antimony .....	Sb	120	Nickel.....	Ni	58·7*
Argon (?) .....	A	40	Niobium.....	Nb	94
Arsenic .....	As	75	Nitrogen.....	N	14·04
Barium .....	Ba	137·4	Osmium .....	Os	191
Beryllium .....	Be	9·1	Oxygen .....	O	16·00
Bismuth .....	Bi	208·5*	Palladium .....	Pd	106
Boron .....	B	11	Phosphorus .....	P	31·0
Bromine .....	Br	79·96	Platinum .....	Pt	194·8
Cadmium .....	Cd	112	Potassium .....	K	39·15
Cæsium .....	Cs	133	Praseodymium (?)	Pr	140
Calcium .....	Ca	40	Rhodium.....	Rh	103·0
Carbon .....	C	12·00	Rubidium .....	Rb	85·4
Cerium .....	Ce	140	Ruthenium.....	Ru	101·7
Chlorine .....	Cl	35·45	Samarium (?).....	Sa	150
Chromium .....	Cr	52·1	Scandium .....	Sc	44·1
Cobalt.....	Co	59	Selenium .....	Se	79·1
Copper .....	Cu	63·6	Silicon .....	Si	28·4
Erbium (?) .....	Er	166	Silver .....	Ag	107·93
Fluorine .....	F	19	Sodium .....	Na	23·05
Gallium .....	Ga	70	Strontium .....	Sr	87·6
Germanium .....	Ge	72	Sulphur .....	S	32·06
Gold .....	Au	197·2	Tantalum .....	Ta	183
Helium (?) .....	He	4	Tellurium .....	Te	127
Hydrogen .....	H	1·01	Thallium .....	Tl	204·1
Indium .....	In	114	Thorium.....	Th	232
Iodine.....	I	126·85	Tin .....	Sn	118·5*
Iridium .....	Ir	193·0	Titanium .....	Ti	48·1
Iron.....	Fe	56·0	Tungsten .....	W	184
Lanthanum .....	La	138	Uranium .....	U	239·5
Lead .....	Pb	206·9	Vanadium .....	V	51·2
Lithium .....	Li	7·03	Ytterbium .....	Yb	173
Magnesium .....	Mg	24·36	Yttrium .....	Y	89
Manganese.....	Mn	55·0	Zinc.....	Zn	65·4
Mercury .....	Hg	200·3	Zirconium .....	Zr	90·6
Molybdenum .....	Mo	96·0			

The numbers in the above table may be regarded as correct to the last figure given, with the exception of those marked by an asterisk. The atomic weight of nickel is certainly lower than that of cobalt, but the number 58·7 is only correct to  $\pm 0\cdot2$ . A like uncertainty holds for bismuth and tin. For hydrogen, the value 1·008 is only certain to 0·001. For practical purposes, the number 1·01 may, therefore, be taken, the error being only about one-fifth per cent.

H. C.

**Gas Generator.** By EMIL JÄGER (*Zeit. angew. Chem.*, 1898, 961).—The apparatus, of which a drawing is given in the paper, consists essentially of a kind of large wine-glass, but having perforations through the bottom, containing the substance to be acted on and placed at the bottom of a cylindrical glass vessel containing acid. Over it is placed a double bell-jar; the inner smaller one which plays the part of a diving bell may be lifted up and down by means of a glass rod attached to it. When down, the acid is completely excluded, when up, the acid ascends and acts on the substance. The strength of the gaseous current is regulated by a screw-clamp attached to a piece of india-rubber connected with a side tube belonging to the outer bell-jar.

The advantage claimed is that, when out of use, not the slightest evolution of gas takes place, even when the screw-clamp is loosened.

L. DE K.

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## Inorganic Chemistry.

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**Quantitative Synthesis of Water.** By EDWARD H. KEISER (*Amer. Chem. J.*, 1898, 20, 733—739. Compare Abstr., 1887, 1078; 1891, 1154).—By the following method, the quantities of hydrogen and oxygen combining to form water can be determined gravimetrically without the necessity of gasometric measurement. A light glass cylinder, terminated at the bottom by a narrow tube carrying a glass stopcock, and closed at the top with a round glass cap with a three-way stopcock, is divided by a slight constriction into two compartments, the smaller and lower of which contains purified phosphoric anhydride. After completely exhausting the tube, it is weighed, and pure spongy palladium, contained in a thin glass tube having a number of small holes near the bottom, is introduced into the larger compartment; the tube is again exhausted and weighed; pure hydrogen is admitted so as to completely saturate the palladium, and after partially exhausting, the amount of hydrogen absorbed is determined. Pure oxygen is then passed through the apparatus at such a rate that the water formed is completely absorbed by the anhydride, and the temperature does not rise sensibly. After completely oxidising the hydrogen, the excess of oxygen is removed by exhausting the apparatus, and the weight of the water formed is determined.

In the author's experiments, the tube used was counterpoised during

all weighings by a duplicate; both the oxygen and hydrogen were prepared electrolytically, and were purified by being passed over heated palladium, and subsequently through tubes of fused caustic potash and phosphoric anhydride. The average of four experiments carried out by this method, ranging from 15·874—15·886, gives 15·880 as the atomic weight of oxygen. W. A. D.

**Electrolytic Production of Chlorates, Bromates, Iodates, and Hypochlorites.** By WILHELM VAUBEL (*Chem. Zeit.*, 1898, 22, 331).—The author finds, on employing an electrolytic cell containing a saturated solution of sodium hydrogen carbonate surrounding the anode, and separated by a porous diaphragm from a strong brine solution in contact with the cathode, that the whole of the chlorine migrating into the anodic compartment is oxidised to chlorate, whilst carbonic anhydride and caustic soda are obtained at the anode and cathode respectively.

The temperature is maintained at 60—70° during electrolysis, and a current density of 5—10 ampères per sq. dcm. and an E.M.F. of 4—5 volts are employed.

A table showing the yield of chlorate after the expiration of certain ampère-hours is given, and the author compares his results with those of previous investigators.

The experimental conditions for the production of potassium chlorate are quite similar, as are also those for the preparation of bromates and iodates. When the above electrolysis is performed at lower temperatures, hypochlorite, and not chlorate, becomes the chief product, but, as in the former experiment, there is no formation of chloride round the anode. G. T. M.

**Electrolytic Preparation of Perchloric Acid and its Salts.** By FRITZ FOERSTER (*Zeit. Elektrochem.*, 1898, 4, 386).—Potassium chlorate in neutral or alkaline solution is scarcely reduced by a high cathodic current density when the cathode is made of platinum, lead, copper, zinc, or nickel, but is vigorously reduced when it is of iron and to some extent when it is of cobalt. In neutral or acid solutions, chlorates are readily oxidised at the anode to perchlorates. A series of experiments shows that, with high current density, concentrated solutions, and low temperatures, the yield of perchlorate is a very good one. A 50 per cent. solution of sodium chlorate was electrolysed with equal platinum electrodes 1·5 cm. apart and a current density of 8·3 ampères per sq. dcm. The solution was at the ordinary temperature, and 4·5 volts were required. The yield increased from 86 to 98 per cent. of the theoretical amount, falling off only when the greater part of the chlorate was oxidised.

With a 5·6 per cent. solution of potassium chlorate and 8 ampères per sq. dcm. the yield was about 82 per cent., but fell off considerably when about one-half of the chlorate was oxidised. In alkaline solutions, oxidation is observed at the beginning of the electrolysis, but even with high current densities it soon ceases, so that the direct production of perchlorates from chlorides would appear to be impracticable. T. E.

**Electrolysis of Solutions of Calcium Chloride.** By H. BISCHOFF and FRITZ FOERSTER (*Zeit Elektrochem.*, 1898, 4, 464).—Oettel's statement that a better yield of chlorate is obtained in the electrolysis of calcium chloride than in that of potassium chloride is confirmed. Measurements of the gases evolved during the electrolysis give the percentages of the current employed (a) in the formation of hypochlorite, chlorate, and perchlorate, (b) in reducing hypochlorite at the cathode, (c) in decomposing water. When a solution of 74.3 grams of calcium chloride in 500 c.c. of water is electrolysed with 6.7 volts, and current densities of 9.1 ampères per sq. dcm. at the anode and 13 ampères per sq. dcm. at the cathode, 85.7 to 90.4 per cent. of the current yields oxygen compounds of chlorine, mainly chlorate, 1.4 to 2.9 per cent. reduces hypochlorite, and 7.8 to 12.8 per cent. decomposes water. With a solution of 100 grams of potassium chloride + 7.5 grams of potash in 500 c.c. of water, the E.M.F. being 4.8 volts and the current densities the same as before, the corresponding values were 50.9 to 61.9, 12 to 19.9 and 20.8 to 29.6. Both solutions were cooled with ice. A solution of barium chloride gave results very similar to those obtained with potassium chloride. The small reduction observed with calcium chloride is probably due to a layer of calcium hydroxide on the cathode which acts as a diaphragm; the greater part of the calcium hydroxide formed combines with chlorine, but part of it remains undissolved, free hypochlorous acid existing in the solution and volatilising with the gases evolved. Further experiments show that at 20—25° the best yield of chlorate is obtained from solutions containing at least (preferably much more than) 10 per cent. of calcium chloride, and with a current density of 10 amperes per sq. dcm. at the anode and at least double that amount at the cathode; the yield is nearly 90 per cent. The deposit of calcium hydroxide on the cathode considerably increases the E.M.F. required; at 50°, however, 4.55 volts suffice, and the yield is but slightly reduced (80 to 87 per cent.). Determinations of oxygen in admixture with hydrogen should not be made in the phosphorus pipette, but by means of copper in presence of a solution of ammonia. T. E.

**Density and Molecular Weight of Ozone.** By ALBERT LADENBURG (*Ber.*, 1898, 31, 2830—2831. Compare this vol., ii, 18).—The calculation of the amount of ozone present in the gas employed in the experiments previously described was based on the assumption that 253.06 parts of iodine are liberated by 48 parts of ozone. Since the object of the experiment was to determine the molecular weight of ozone, the author has recalculated the results on the simpler assumption that 1 molecule of iodine is set free by 1 molecule of ozone. He thus finds that the gas employed contained 84.4 per cent. by weight of ozone, and that the density of ozone is 1.469. A. H.

**Colour of Sulphur Vapour.** By J. LEWIS HOWE and S. G. HAMNER (*J. Amer. Chem. Soc.*, 1898, 20, 757—759).—The authors, after referring to the varying statements with regard to the colour of sulphur vapour, describe experiments which show that this colour varies with the temperature, being orange-yellow just above the boiling point of sulphur, becoming rapidly darker with rise of temperature

until it becomes deep red comparable to the red of ferric thiocyanate ; this red colour is most intense at about  $500^{\circ}$ . Above this temperature, the colour becomes lighter until at  $634^{\circ}$ , the limit of temperature at which observations were made, the colour is straw-yellow.

G. W. F. H.

**The Change in Sulphur by Heat.** By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1898, 18, 365—370).—The author has determined the amount of insoluble sulphur which is formed on heating sulphur at known temperatures for a known time. The sulphur, previously crystallised from carbon bisulphide, is sealed up in a vacuum in a glass tube, and, after heating, the insoluble portion is determined by extraction with carbon bisulphide (so-called insoluble sulphur is slightly soluble in carbon bisulphide). When heated at  $141.7^{\circ}$ , about 5.2 per cent. of insoluble sulphur is formed, the amount formed being independent of the time ; after 1 hour, this amount is approximately the same as after 16 hours. When heated at  $183^{\circ}$ , the amount of insoluble sulphur is also independent of the time, and also apparently of the temperature, since about 6 per cent. of insoluble sulphur was obtained. When heated at  $448^{\circ}$  for 15 minutes and then gradually cooled, 1.8 to 3.3 per cent. of insoluble sulphur is formed ; when, however, the molten sulphur is suddenly cooled by plunging into cold water, 30.9 to 34.2 per cent. of insoluble is obtained. The formation of the insoluble modification and the converse formation of soluble sulphur take place, therefore, with extreme rapidity, so that the amount of insoluble sulphur which is present after crystallisation is not dependent on the temperature and time of the heating, but on the rate of the crystallisation and the temperature at which it takes place. Therefore, different samples of sulphur which have been heated for different times above the melting point after remaining some time at a lower temperature ( $100^{\circ}$ ), are practically identical as regards the concentration of the insoluble modification, from which it follows that the difference observed in the velocity of solidification, &c., must be assigned to some other cause than the different concentration of the insoluble modification (Abstr., 1897, ii, 439).

A sample of insoluble sulphur which has been kept for 5 months, when treated with carbon bisulphide, gives the same percentage of soluble matter as when freshly prepared. On evaporating the solution, the sulphur separates in solid drops which show no signs of crystallisation under the microscope, but give evidence of crystallisation when subjected to polarised light. This sulphur is not completely soluble in carbon bisulphide, so that the "insoluble" modification, when dissolved, is not completely converted into the soluble modification. The author concludes that the soluble and insoluble modifications have different molecules in solution, that they are not only physical isomerides, but chemical isomerides, having a relation to each other similar to that of ozone to oxygen.

E. C. R.

**Azoimide.** By THEODOR CURTIUS and JOHANNES RISSOM (*J. pr. Chem.*, 1898, [ii], 58, 261—309. Compare Abstr., 1891, 57 ; 1892, 112).—The azoimide,  $\text{HN}_3$ , was obtained in aqueous solution by distilling with dilute sulphuric acid either the ammonium salt (Abstr.,



1892, 113) or the lead salt precipitated from the mother liquor of that salt; excess of acid should be avoided, especially in the latter case. Azoimide is decomposed but very slowly when boiled with dilute hydrochloric acid; most of the nitrogen is liberated as the gas; a little ammonia is formed, but neither hydroxylamine nor hydrazine. In aqueous solution at the ordinary temperature, azoimide is very stable; such loss of strength as does occur is due to volatilisation.

The metallic salts (azoimides, azides, or nitrides) were prepared (1) by precipitation, in the case of  $\text{AgN}_3$ ,  $\text{HgN}_3$ ,  $\text{Pb}(\text{N}_3)_2$ ,  $\text{TlN}_3$ , and  $\text{Cu}(\text{N}_3)_2$ ; (2) by dissolving the metal in the dilute acid of 16–17 per cent. strength (applicable in the case of Zn, Fe, Cd, and Mn, but the solutions are decomposed on evaporation, basic azoimides or even the hydroxides of the metal being formed and azoimide given off); (3) by dissolving the freshly precipitated hydroxide or carbonate of the metal in the aqueous acid and evaporating the solution; (4) by double decomposition of the sulphate of the metal with barium azoimide and evaporation of the filtered solution. In the analysis of the salts, the nitrogen was sometimes determined by combustion, the substance being mixed with plenty of powdered lead chromate in a long porcelain boat, but more often by distillation with dilute sulphuric acid, the azoimide evolved being collected in excess of N/10 potassium hydroxide, of which the excess was estimated with N/10 hydrochloric acid, phenolphthalein serving as the indicator; in the residue from the distillation, the metal was determined. Crystallographically the azoimides of potassium, rubidium, and thallium appear to form an isomorphous tetragonal group, those of barium, calcium (and strontium?) an isomorphous rhombic one; in all cases, the double refraction is very marked. As regards solubility in water at 16°, the azoimides of Na, K, Rb, Cs,  $\text{NH}_4$  arrange themselves, as compared with the corresponding halogen salts, in the order of increasing solubility F, Cl,  $\text{N}_3$ , Br, I (which is also that of increasing formula-weight), those of Ba, Ca, Sr, Li, Tl in the order F,  $\text{N}_3$ , Cl, Br, I. When the azoimides of the alkali and alkaline earth metals are heated in a small capillary tube closed at one end (melting point tube), azoimide is evolved, and the metal is left (in this way, small quantities of Cs, Rb, Ba, Sr, Ca may be prepared); none of them are very explosive, only lithium and the alkaline earth azoimides exploding at comparatively low temperatures, and only thallium azoimide when hammered; in aqueous solution, they attack glass, although the acid itself has no such action; in aqueous solution, they are stable, but the solution has often an alkaline reaction. The azoimides of the heavy metals are often very explosive, perhaps most of all the potassium-platinum derivative, which explodes spontaneously with frightful violence, even in aqueous solution. No azoimide has been found as yet to crystallise with water.

Ammonium azoimide,  $\text{NH}_4 \cdot \text{N}_3$ , melts and decomposes violently at 160°; very volatile; the vapour density at 100° in Hofmann apparatus gave the molecular weight = 29.3; 30.2 (calculated 60), so that complete dissociation must have taken place; the spectrum resembles that of ammonium chloride, showing the hydrogen lines and the red-yellow part of the nitrogen spectrum; crystals apparently rhombic. Hydrazine

azoimide,  $N_2H_5 \cdot N_3$ , begins to melt at  $65^\circ$ , and decomposes energetically at  $108^\circ$ . *Lithium azoimide*,  $LiN_3$ : crystals anisotropic; deliquescent; explodes between  $115^\circ$  and  $298^\circ$ . *Sodium azoimide*,  $NaN_3$ : crystals apparently hexagonal; unchanged at  $350^\circ$ . *Potassium azoimide*,  $KN_3$ : crystals tetragonal ( $a:c = 1:0.5810$ ); melts and decomposes above  $350^\circ$ . *Rubidium azoimide*,  $RbN_3$ : the best crystallised of the salts examined; crystals tetragonal ( $a:c = 1:0.5785$ ); slightly hygroscopic; melts at  $330-340^\circ$ . *Cesium azoimide*,  $CsN_3$ , crystalline, deliquescent; melts at  $310-318^\circ$ . *Thallium azoimide*,  $TlN_3$ : crystals, tetragonal ( $a:c = 1:0.588$ ); explodes when struck, also when heated strongly, but is unchanged at  $340^\circ$ .

*Calcium azoimide*,  $Ca(N_3)_2$ : crystals rhombic ( $a:b:c = 0.3207:1:0.8815$  (?)); hygroscopic; explodes at  $144-156^\circ$ . *Strontium azoimide*,  $Sr(N_3)_2$ : crystalline; hygroscopic; decomposes violently at  $194-196^\circ$ . *Barium azoimide*,  $Ba(N_3)_2$ : crystals rhombic ( $a:b:c = 0.3424:1:0.8461$ ); hardly hygroscopic; decomposes violently at  $217-221^\circ$ .

*Magnesium* and *beryllium azoimides* are readily decomposed by hot water. *Basic zinc azoimide*,  $N_3 \cdot Zn \cdot OH$  (?); crystals ill-defined, anisotropic. *Basic manganese azoimide*,  $N_3 \cdot Mn \cdot OH$ .

*Cadmium azoimide*,  $Cd(N_3)_2$ : yellow, biaxial crystals; forms with pyridine a colourless, crystalline compound,  $Cd(N_3)_2 \cdot 2C_5NH_5$ . *Cupric azoimide*,  $Cu(N_3)_2$ , from copper sulphate and sodium azoimide, but also by dissolving copper in the aqueous acid; dark brown and crystalline; insoluble in water; very explosive.

Aluminium forms no azoimide; from a solution of the sulphate, sodium azoimide precipitates the hydroxide. Chromium azoimide is formed in solution by dissolving chromium hydroxide in aqueous azoimide; it decomposes on evaporating the solution, the residue containing only  $2N_3$  per  $3Cr$ . Ferrous sulphate gives a colourless solution with cold aqueous azoimide; on boiling, a yellow solid is precipitated. The solution turns red when shaken in the air; a deep red solution is also obtained when solutions of ferric chloride and azoimide are mixed; this becomes colourless slowly in the cold, rapidly when boiled, all the iron being precipitated.

Tin is precipitated from a solution of stannous chloride by sodium azoimide, and the precipitate is, in part at any rate, an azoimide.

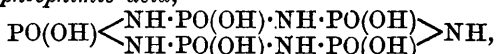
*Basic nickel azoimide*,  $N_3 \cdot Ni \cdot OH$ , with some  $Ni(N_3)_2$  (?), from nickel carbonate and aqueous azoimide: green, crystalline; explodes at  $247-271^\circ$ . *Basic cobalt azoimide*,  $N_3 \cdot Co \cdot OH$ , with some  $Co(N_3)_2$ : violet and possibly amorphous; *potassium cobaltoazoimide*,  $KN_3 \cdot Co(N_3)_2$ , precipitated when strong solutions of the two azoimides are mixed, is bright blue (gives a pink solution) and crystalline, and explodes at  $225^\circ$ ; the *ammonium* analogue,  $(NH_4)N_3 \cdot (CoN_3)_2$ , is similar in appearance and properties. An analogous bright green nickel compound,  $KN_3 \cdot Ni(N_3)_2$  (?), also crystalline and explosive, was obtained.

By mixing strong solutions of platinochloric acid and potassium azoimide, or aurochloric acid and sodium azoimide, solutions were obtained from which, in the first case, a brownish-red, in the second an orange crystalline, residue, extremely explosive in both cases, remained on evaporation (potassium platinoazoimide and sodium auroazoimide ?).

C. F. B.

**Metaphosphimic Acids. III.** By HENRY N. STOKES (*Amer. Chem. J.*, 1898, 20, 740—760 and *Zeit. Anorg. Chem.*, 19, 36—58. Compare Abstr., 1897, ii, 28 and 94).—Although penta- and hexa-phosphonitrilic chlorides (Abstr., 1898, ii, 70), on hydrolysis give rise to the corresponding penta- and hexa-metaphosphimic acids, from heptaphosphonitrilic chloride the acid  $(\text{H}_2\text{PNO}_2)_7 + \text{H}_2\text{O}$  is obtained. The salts of all three new acids differ from those of tri- and tetra-metaphosphimic acid in being amorphous; hence, in many cases, they cannot be obtained satisfactorily pure.

*Pentametaphosphimic acid,*



is best prepared by shaking pentaphosphonitrilic chloride (4 parts), dissolved in ether free from alcohol (20 parts), with a solution of sodium hydroxide (5 parts) in water (20 parts) during 50 hours. On adding alcohol, the *pentasodium* salt,  $\text{P}_5\text{N}_5\text{O}_{10}\text{H}_5\text{Na}_5 + 2\text{H}_2\text{O}$ , is precipitated as a thick syrup, which is washed repeatedly with 60 per cent. alcohol, dissolved in water, reprecipitated by alcohol and again washed until free from sodium chloride; it is then freed from water by stirring several hours with frequently renewed absolute alcohol. Thus prepared, it is a white, sandy powder, which retains  $2\text{H}_2\text{O}$  after drying at  $100^\circ$ , and dissolves in water with development of heat, the solution having an alkaline reaction. When dissolved in 80 per cent. acetic acid, it is converted into the *tetrasodium* salt,  $\text{P}_5\text{N}_5\text{O}_{10}\text{H}_6\text{Na}_4 + 2\text{H}_2\text{O}$ ; the latter is precipitated on adding alcohol and resembles the pentasodium salt, but has a neutral reaction. On adding a magnesium salt to an aqueous solution of sodium pentametaphosphimate strongly acidified with acetic acid, the *magnesium* salt,  $\text{P}_5\text{N}_5\text{O}_{10}\text{H}_6\text{Mg}_2 + 5\text{H}_2\text{O}$ , is precipitated; on dissolving this in dilute nitric acid, adding ammonia until a precipitate just forms, and filtering, a solution containing the *salt*  $(\text{P}_5\text{N}_5\text{O}_{10}\text{H}_6)_2\text{Mg}$  is obtained. The silver salt,  $\text{P}_5\text{N}_5\text{O}_{10}\text{H}_5\text{Ag}_5$ , precipitated by adding the calculated quantities of nitric acid and silver nitrate to a solution of the tetrasodium salt, is a white powder, which is not affected by light or by heating at  $100^\circ$ ; it is decomposed, however, by cold caustic alkalis. Salts containing more than five atoms of silver can be obtained, which are yellow in colour. When silver nitrate is added to an ammoniacal solution of sodium pentametaphosphimate, a yellow, amorphous *salt*,  $\text{P}_5\text{N}_5\text{O}_{11}\text{H}_3\text{Ag}_9$ , is obtained, which is probably a derivative of *amidotetrimidopentaphosphoric acid*,  $\text{OH} \cdot \text{PO}(\text{NH}_2) \cdot [\text{NH} \cdot \text{PO}(\text{OH})]_3 \cdot \text{NH} \cdot \text{PO}(\text{OH})_2$ . Somewhat impure pentametaphosphimic acid separates as a gelatinous precipitate on adding alcohol to the filtrate obtained after decomposing its silver salt with hydrogen sulphide.

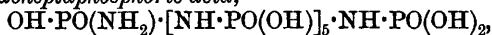
When sodium pentametaphosphimate is heated during 8 hours with dilute acetic acid, it is decomposed into a mixture of the sodium salts of tetrametaphosphimic acid (Abstr., 1897, ii, 94), tri-imidotetraphosphoric di-imidotriphosphoric and orthophosphoric acids, together with other substances. The first of these acids is completely precipitated during the reaction as a sparingly soluble *acid sodium* salt, in spindle-shaped crystals. On concentrating the filtrate, and adding sodium acetate, *sodium tri-imidotetraphosphate*, probably  $\text{P}_4\text{N}_3\text{O}_{10}\text{H}_5\text{Na}_4$ , crystallises out in small rhombic or hexagonal plates; on dissolving in

water and adding silver nitrate, the *silver* salt,  $P_4N_3O_{10}H_5Ag_4$ , separates as an amorphous precipitate which becomes crystalline on washing with water.

*Sodium hexametaphosphimate*,  $P_6N_6O_{12}H_6Na_6 + 2H_2O$ , prepared from hexaphosphonitrilic chloride, closely resembles sodium pentameta-phosphimate. No definite magnesium salt could be obtained, but the *silver* salt,  $P_6N_6O_{12}H_6Ag_6$ , separates on adding the calculated quantity of nitric acid and silver nitrate to a solution of the sodium salt; it forms a white, gelatinous precipitate, and is decomposed by cold caustic potash. In presence of ammonia, a yellow *silver* salt is precipitated. Free hexametaphosphimic acid cannot be obtained, as on decomposing its silver salt suspended in water by hydrogen sulphide, filtering, and adding alcohol, no precipitate separates; on attempting to evaporate, decomposition occurs, and a gum-like residue is obtained.

On heating sodium hexametaphosphimate with dilute acetic acid, 30 per cent. of the theoretical quantity of tetrametaphosphimic acid is obtained.

When the hydrolysis of heptaphosphonitrilic chloride is effected by sodium hydroxide as in the case of pentaphosphonitrilic chloride, *amidoheximidoheptaphosphoric acid*,



is formed; the *sodium* salt,  $P_7N_7O_{15}H_8 \cdot 57Na_{7 \cdot 43} + 2H_5O$ , and the *silver* salt,  $P_7N_7O_{15}H_9Ag_7$ , were analysed.

Attempts to prepare amides by acting on ethereal solutions of tetra- and penta-phosphonitrilic chloride with aqueous ammonia gave amorphous substances of indefinite composition.

In discussing his results, the author points out that tetrametaphosphimic acid is by far the most stable of the metaphosphimic acids. To explain this, and the formation of tetraphosphimic acid from the penta- and hexa-acids by hydrolysis, a hypothesis as to the stability of the acid rings is put forward, which is similar to von Baeyer's tension theory of carbon rings. W. A. D.

**Atmospheric Carbonic Anhydride.** By ALBERT LÉVY and H. HENRIET (*Compt. rend.*, 1898, 127, 353—355).—When air that has been completely freed from carbonic anhydride by passing it over potassium hydroxide is allowed to remain for 2 hours in contact with potassium hydroxide solution, a further quantity of carbonic anhydride is formed (compare Abstr., 1898, ii, 573). If the potassium hydroxide solution contains 7 grams per litre, all the carbonic anhydride existing as such in the air is completely absorbed in 10 minutes, and all the organic matter in the air in the form of gas or vapour is completely oxidised in 2 hours.

Experiments were made during July, 1898, in which the carbonic anhydride absorbed by the potassium hydroxide was determined after it had been in contact with the air in large flasks for 10 minutes and 2 hours respectively. The difference was often from 3 to 5 litres per 100 cubic metres of air, but sometimes was as high as 11 or 12 litres, and in one exceptional instance it reached 56 litres. It is obvious that this difference gives useful information as to the quantity of gaseous organic matter present in the air. In all cases, the difference observed

in the manner indicated is somewhat less than its true value, because even in 10 minutes the organic matter is appreciably oxidised in presence of the alkali.

C. H. B.

**The Various Theories relating to the Constitution of the Ammonio-metallic Salts.** By FRITZ REITZENSTEIN (*Zeit. anorg. Chem.*, 1898, 18, 152—210).—An historical review of the theories that have been put forward on this subject.

E. C. R.

**Solutions of Silicates of the Alkalis.** By LOUIS KAHLENBERG and AZARIAH T. LINCOLN (*J. Physical Chem.*, 1898, 2, 77—90).—The conclusion arrived at by Kohlrausch (*Abstr.*, 1893, ii, 166) that in solutions of sodium silicates these salts are hydrolytically decomposed into sodium hydroxide and colloidal silicic acid, has been confirmed by investigating the freezing points of such solutions. The freezing points and the electrical conductivity of solutions of the silicates of potassium, lithium, rubidium, and caesium show that these salts are also decomposed by water into colloidal silicic acid and the hydroxide of the alkali metal. The silicates of the alkalis all show an analogous behaviour when dissolved in water. The same solution is obtained whether a silicate is dissolved in water, or whether solutions of caustic alkali and colloidal silicic acid in proper proportions are mixed. Since colloidal silicic acid has but little effect on the freezing point, the degree of hydrolytic decomposition of the silicates can be calculated from the lowering of the freezing point of their solutions. Silicates of the general formulæ  $M_2SiO_3$  and  $MHSiO_3$  are practically completely hydrolytically dissociated when one gram-molecule is contained in 48 litres. Silicates of the general formula  $M_2Si_5O_{11}$  are practically completely decomposed by water when one gram-molecule is present in 128 litres. A comparison of the electrical conductivity of silicate solutions with that of solutions of the alkali hydroxides shows that the values of the former approach the latter as the solutions become more dilute, the retarding influence that the silicic acid has on the mobility of the ions gradually becoming less.

From the results of the above investigations, it appears safe to conclude that, in natural waters, silicic acid always occurs in the colloidal state; only in very rare instances are the solutions of the silicates so concentrated that they are not practically completely hydrolytically decomposed.

H. C.

**Sodium Oxides.** By ROBERT DE FORCRAND (*Compt. rend.*, 1898, 127, 364—366).—When dry air, free from carbonic anhydride, is passed through sodium heated somewhat above its melting point, the first product is a bulky, grey, arborescent mass, consisting of the suboxide  $Na_3O$ , mixed with a small proportion of sodium. If the heating is continued, this substance burns, and is converted into a yellow mixture of the monoxide and dioxide, or completely into the dioxide  $Na_2O_2$ , which, however, generally retains a small proportion of water. No trioxide is formed.

The suboxide does not rapidly absorb water vapour, but is gradually oxidised when exposed to air; if thrown into water, it reacts violently, with liberation of pure hydrogen.

C. H. B.

**Interaction of Sodium Arsenite and Sodium Thiosulphate.** By LEROY W. McCAY (*Chem. News*, 1898, 78, 209).—When sodium thiosulphate and sodium arsenite in the theoretical quantities are made into a thick paste with caustic soda and rubbed in a mortar, the following change takes place:  $\text{Na}_3\text{AsO}_3 + \text{Na}_2\text{S}_2\text{O}_3 = \text{Na}_3\text{AsO}_3\text{S} + \text{Na}_2\text{SO}_3$ . The sodium orthomonothioxyarsenate is separated by treating the paste with water, filtering, and crystallising. It is generally obtained by similar treatment of a paste of sulphur, caustic soda, and arsenious oxide in stöchiometrical amounts. D. A. L.

**Saline Efflorescence of Walls.** By H. VAN ERP (*Rec. Trav. Chim.*, 1898, 17, 296—299).—As a rule, the efflorescence formed on walls consists almost entirely of sodium sulphate and carbonate, with varying quantities of water of crystallisation; nitrates, nitrites, phosphates, and ammonium salts can seldom be detected, but calcium carbonate and sand are usually present. In the case of a wall of a corridor in the Harlem Museum, which had been covered for some time with a curtain, it was found that, beneath the latter, a deposit of slender needles, several centimetres in length, of pure sodium sulphate (with  $10\text{H}_2\text{O}$ ) had formed. W. A. D.

**Ammoniacal Lithium Chlorides.** By J. BONNEFOI (*Compt. rend.*, 1898, 127, 367—369).—The compound  $\text{LiCl}\cdot\text{NH}_3$  is formed by the action of dry ammonia on pure and dry lithium chloride at a temperature exceeding  $85^\circ$ , or by heating the compounds containing a higher proportion of ammonia. Its heat of dissolution at  $15^\circ$  is  $+5\cdot385$  Cal. and hence,  $\text{LiCl sol.} + \text{NH}_3 \text{ gas} = \text{LiCl}\cdot\text{NH}_3 \text{ sol.}$  develops  $+11\cdot842$  Cal. Its vapour pressures are as follows.

<i>t</i>	$88^\circ$	$96^\circ$	$109\cdot2^\circ$	$119^\circ$
<i>p</i>	256 mm.	367 mm.	646 mm.	975 mm.

and the heat of formation calculated by Clapeyron's formula agrees closely with the number directly determined.

The compound  $\text{LiCl}\cdot 2\text{NH}_3$  is obtained by the action of ammonia on lithium chloride between  $60^\circ$  and  $85^\circ$ , or by heating the higher compounds between these limits. Its heat of dissolution is  $+2\cdot668$  Cal. hence,  $\text{LiCl sol.} + 2\text{NH}_3 \text{ gas} = \text{LiCl}\cdot 2\text{NH}_3 \text{ sol.}$  develops  $+23\cdot359$  Cal. Its vapour pressures are

<i>t</i>	$68\cdot8^\circ$	$77^\circ$	$83^\circ$	$89\cdot2^\circ$
<i>p</i>	373 mm.	558 mm.	739 mm.	980 mm.

The compound  $\text{LiCl}\cdot 3\text{NH}_3$  is formed between  $20^\circ$  and  $60^\circ$ . Its vapour pressures are

<i>t</i>	$43^\circ$	$50^\circ$	$60^\circ$	$62\cdot2^\circ$	$65^\circ$
<i>p</i>	320 mm.	473 mm.	790 mm.	882 mm.	1011 mm.

The compound  $\text{LiCl}\cdot 4\text{NH}_3$  is formed below  $13^\circ$ ; its heat of dissolution is  $+0\cdot292$  Cal., hence  $\text{LiCl sol.} + 4\text{NH}_3 \text{ gas} = \text{LiCl}\cdot 4\text{NH}_3 \text{ sol.}$  develops  $+43\cdot335$  Cal.,  $\text{LiCl}\cdot 3\text{NH}_3 \text{ sol.} + \text{NH}_3 \text{ gas} = \text{LiCl}\cdot 4\text{NH}_3 \text{ sol.}$  develops  $+8\cdot879$  Cal. Its vapour pressures are

<i>t</i>	$0^\circ$	$9^\circ$	$14\cdot5^\circ$
<i>p</i>	384 mm.	640 mm.	850 mm.

The heat developed by the combination of the four successive molecules of ammonia with the lithium chloride is +11·843, +11·517, +11·097, and +8·879 Cals. respectively.

In all cases, Clapeyron's formula gives results that agree with the direct determinations (compare Abstr., 1897, ii, 371). C. H. B.

**Dicalcium Phosphate.** By A. BARILLÉ (*Chem. Centr.*, 1898, i, 434—435; from *Rép. Pharm.*, 1897, 529).—When ammonia is added to a solution of monocalcium phosphate, half the phosphoric acid remains in solution as ammonium phosphate, and dicalcium phosphate is precipitated. By adding calcium chloride solution to the filtrate, the rest of the phosphoric acid is precipitated as monocalcium phosphate. According to the author, the latter reaction takes place in three phases. Ammonium chloride, tricalcium phosphate, and tetrahydrogen calcium phosphate are first formed, then by the action of water the last compound forms tricalcium phosphate and phosphoric acid, and finally the whole of the tricalcium phosphate acts on the phosphoric acid to form monocalcium phosphate.

To prepare dicalcium phosphate, 1000 grams of well burnt bone ash are stirred with hot water and then gradually mixed with 1454 grams of commercial hydrochloric acid of sp. gr. = 1·17. When the action is completed, 3 litres of hot water are added, the solution of monocalcium phosphate and calcium chloride is filtered, the filtrate diluted to 10 litres and a mixture of 442 grams of ammonia of sp. gr. = 0·925 with 20 times its weight of water is slowly added. The precipitated dicalcium phosphate, after collecting, washing with water until free from acid and drying at 60°, is a light, snow-white, lustrous powder, which consists of flat, hexagonal crystals. Dicalcium phosphate crystallises with 4H<sub>2</sub>O. Its solution is not decomposed by boiling or evaporating, and its saturated solution in water containing carbonic anhydride contains 0·069 per cent. of the salt, and might be used medicinally instead of tricalcium phosphate. E. W. W.

**Crystallisation of Anhydrous Calcium and Strontium Sulphides.** By A. MOURLOT (*Compt. rend.*, 1898, 127, 408—410).—Calcium or strontium sulphide can be obtained in a crystalline condition by heating a moderately large quantity of a mixture of the corresponding sulphate with carbon for a few minutes only in an electric furnace with a current of 1000 ampères and 60 volts. If the amorphous sulphides are heated in a carbon dish in an electric tube furnace until they are completely melted, they crystallise on cooling. Both sulphides crystallise in the cubic system; the sp. gr. of the calcium compound = 2·8 at 15°, and of the strontium compound = 3·7 at 15°. In chemical properties, they closely resemble anhydrous barium sulphide (Abstr., 1898, ii, 376). C. H. B.

**Composition of Phosphorescent Strontium Sulphides.** By JOSÉ R. MOURELO (*Compt. rend.*, 1898, 127, 229—231).—Strontium sulphide, prepared from minerals, contains strontium sulphate, in quantity depending on the degree of exposure to air, and also small quantities of sodium chloride; it may also contain calcium, barium, iron, and aluminium compounds. When prepared from pure strontium

sulphate, carbonate or oxide, it usually contains some sulphate, but if special precautions are taken and it is obtained quite pure, it is non-phosphorescent.  
C. H. B.

**Phosphorescent Strontium Sulphide.** By JOSÉ R. MOURELO (*Compt. rend.*, 1898, 127, 372—374).—Strontium thiosulphate, prepared by the action of sodium thiosulphate on strontium chloride, retains with great tenacity small quantities of sodium chloride, and consequently this salt is present in any strontium sulphide prepared from it by the action of heat; the phosphorescence is yellowish-green, and somewhat intense.

An intensely phosphorescent sulphide is obtained by a method very similar to that adopted by Verneuil for the preparation of calcium sulphide. For 100 grams of strontium carbonate, 2 grams of bismuth subnitrate, 2 grams of sodium carbonate, and 0.12 gram of sodium chloride is taken; after moistening the carbonate with the sodium salts, it is heated to redness, and then mixed with 21 grams of sulphur and the bismuth salt, and heated to bright redness for 4 hours. The product is relatively very stable.  
C. H. B.

**Double Compounds of Cerium Tetrachloride.** By IVAN KOPPEL (*Zeit. anorg. Chem.*, 1898, 18, 305—311).—A solution of cerium tetrachloride is obtained by treating hydrated cerium dioxide, suspended in methylic or ethylic alcohol, with dry hydrogen chloride; it forms a yellowish-brown solution, which deposits yellow, crystalline crusts when evaporated in a vacuum, and decomposes at once, with evolution of chlorine, when removed from the mother liquor or when brought into contact with water. This solution forms stable, double compounds with pyridine, quinoline, and the triethylamine chlorides, but not with mono- or di-ethylamine hydrochloride. In the preparation of these compounds, the author employed commercial cerous oxalate, and he points out that by precipitating the cerium in the form of one of these double salts, a very easy method is obtained for the preparation of pure cerium compounds.

*Dipyridine cerium hexachloride*,  $(C_5NH_5)_2, H_2CeCl_6$ , obtained by adding pyridine hydrochloride to the above solution of cerium tetrachloride and then precipitating with ether, crystallises in small, lustrous, quadratic leaflets, is easily soluble in methylic alcohol, less so in ethylic alcohol, and is at once decomposed by water, with evolution of chlorine.

*Diquinoline cerium hexachloride*,  $(C_9NH_7)_2, H_2CeCl_6$ , obtained in a similar manner to the preceding salt, is a yellow, crystalline precipitate, less soluble than the preceding salt, and at once decomposes when treated with water.

*Di-triethylamine cerium hexachloride*,  $(NEt_3)_2, H_2CeCl_6$ , crystallises well from alcohol in octahedra.

Yellow, crystalline salts, which are probably the double compounds  $K_2CeCl_6$  and  $(NH_4)_2CeCl_6$ , are obtained by adding finely powdered potassium or ammonium carbonate to the solution of cerium tetrachloride containing strong hydrochloric acid, and then shaking with a large quantity of ether; when separated from the solution, they at



once decompose, with evolution of chlorine. The author was unable to obtain double salts with calcium, mercury, or ferric chloride.

E. C. R.

**Praseodymium.** By CARL VON SCHEELÉ (*Zeit. anorg. Chem.*, 1898, 18, 352—364. Compare Abstr., 1898, ii, 519).—*Praseodymium chloride*,  $\text{PrCl}_3 + 7\text{H}_2\text{O}$ , crystallises in large, deliquescent crystals when the concentrated solution is allowed to remain over sulphuric acid; sp. gr. at  $16^\circ = 2.251$ . The *bromide*, with  $6\text{H}_2\text{O}$ , is obtained by dissolving the oxide in hydrobromic acid. The *platinochloride*,  $\text{PrCl}_3, \text{PtCl}_4 + 12\text{H}_2\text{O}$ , crystallises in large, yellow crystals and slowly gives off water when allowed to remain over sulphuric acid. The *platinobromide*, with  $10\text{H}_2\text{O}$ , separates in large, dark red crystals and effloresces when allowed to remain over sulphuric acid. The *aurichloride*, with  $10\text{H}_2\text{O}$ , crystallises in beautiful, deliquescent crystals and is very soluble in water. The *auribromide* crystallises in long needles which deliquesce extremely rapidly on exposure to the air.

*Praseodymium platinocyanide*,  $2\text{Pr}(\text{CN})_3, 3\text{Pt}(\text{CN})_2 + 18\text{H}_2\text{O}$ , obtained by adding the theoretical quantity of praseodymium sulphate to a solution of barium cyanide and platinum cyanide, crystallises in black, fluorescent prisms; it effloresces over sulphuric acid, becoming red, and giving off  $4\text{H}_2\text{O}$ ; sp. gr. at  $16^\circ = 2.663$ .

*Praseodymium nitrate*,  $\text{Pr}(\text{NO}_3)_3 + 6\text{H}_2\text{O}$ , crystallises in long, deliquescent needles. The double *sodium* salt,  $\text{Pr}(\text{NO}_3)_3, 2\text{NaNO}_3 + \text{H}_2\text{O}$ , crystallises in small, deliquescent needles. The *ammonium* salt, with  $4\text{H}_2\text{O}$ , crystallises in large, deliquescent crystals; sp. gr. = 2.155.

*Praseodymium sulphate*,  $\text{Pr}_2\text{SO}_4 + 15\frac{1}{2}\text{H}_2\text{O}$ , is obtained by allowing a dilute solution to crystallise very slowly; it crystallises with  $8\text{H}_2\text{O}$  at the ordinary temperature; sp. gr. = 2.822; and with  $5\text{H}_2\text{O}$  when a saturated solution is concentrated on the water-bath. The anhydrous salt has the sp. gr. = 3.720; 23.64 parts are soluble in 100 parts  $\text{H}_2\text{O}$  at  $0^\circ$ , and 17.7 parts are soluble in 100 parts  $\text{H}_2\text{O}$  at  $20^\circ$ . The double *potassium* salt,  $\text{Pr}_2(\text{SO}_4)_3, 3\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$ , is a heavy, crystalline precipitate, very sparingly soluble in water and easily soluble in hydrochloric and nitric acids; sp. gr. = 3.275. The double *ammonium* salt, with  $8\text{H}_2\text{O}$ , separates in large crystals, is not altered by exposure to the air or by remaining over sulphuric acid, is sparingly soluble in water, and becomes anhydrous when heated at  $170^\circ$ ; sp. gr. = 2.532.

*Praseodymium selenate*,  $\text{Pr}_2(\text{SeO}_4)_3 + 8\text{H}_2\text{O}$ , is obtained by allowing a solution of the oxide in selenic acid to crystallise over sulphuric acid; sp. gr. = 3.094. It crystallises, with  $5\text{H}_2\text{O}$ , in prisms when the solution is concentrated on the water-bath; the *anhydrous* salt is obtained by heating the preceding salt at  $200^\circ$ ; sp. gr. = 4.305. The double *potassium* salt,  $\text{Pr}_2(\text{SeO}_4)_3, 3\text{K}_2\text{SeO}_4 + 4\text{H}_2\text{O}$ , is similar to the corresponding sulphate. A double salt with ammonium selenate could not be obtained.

*Praseodymium dithionate*,  $\text{Pr}_2(\text{S}_2\text{O}_6)_3 + 12\text{H}_2\text{O}$ , obtained from praseodymium sulphate and barium dithionate, crystallises from the syrupy solution when it is exposed over sulphuric acid, rapidly deli-

quescens on exposure to the air, and evolves sulphurous anhydride when warmed.

The *acid selenite*,  $\text{Pr}_2(\text{SeO}_3)_3 \cdot \text{H}_2\text{SeO}_3 + 3\text{H}_2\text{O}$ , obtained by precipitating the sulphate with sodium selenite and then adding a solution of selenic acid, crystallises in slender needles.

The *carbonate*,  $\text{Pr}_2(\text{CO}_3)_3 + 8\text{H}_2\text{O}$ , obtained by treating the hydroxide, suspended in water, with carbonic anhydride, or by precipitating the chloride with ammonium carbonate or potassium hydrogen carbonate, crystallises in small, lustrous scales.

The *oxalate*,  $\text{Pr}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$ , is a crystalline precipitate, soluble in concentrated acids, and does not form double salts with alkaline oxalates. The *acetate*, with  $2\text{H}_2\text{O}$ , crystallises in slender needles at the ordinary temperature, and with  $1\frac{1}{2}\text{H}_2\text{O}$  in small, slender needles at the temperature of the water-bath. The *propionate*, when evaporated over sulphuric acid, crystallises, with  $3\text{H}_2\text{O}$ , in large prisms, and on the water-bath, with  $1\text{H}_2\text{O}$ , in large, thin, lustrous leaflets. E. C. R.

**Behaviour of Thallium in Acid Solution towards Hydrogen Sulphide in Presence of Arsenic, Antimony, and Tin.** By JOSEF LOCZKA (*Chem. Centr.*, 1898, i, 657; from *Magyar Chemiai Folyóirat*, 3).—Thallium is not precipitated by hydrogen sulphide in acid solutions, but in presence of dissolved arsenic, antimony, or tin, red precipitates are formed which contain thallium. The larger the amount of acid present, the less the amount of thallium precipitated, and, with a large excess of acid, no thallium is thrown down. The arsenic precipitate,  $\text{TlAsS}_2$ , occurs naturally in a crystalline form in the realgar from Alchar in Macedonia. E. W. W.

**Action of Water on Metallic Copper and Lead.** By ROBERT MELDRUM (*Chem. News*, 1898, 78, 209—210).—In these experiments, 7 feet of bright copper wire,  $\frac{1}{16}$ -inch in diameter, was exposed, in a test tube, to 100 c.c. of the water; lake water, waters with and without free ammonia, and distilled water were all found to dissolve copper to a certain extent, some hundredths per 100,000 even in 24 hours.

In the lead experiments, pieces of the same lead piping, 2 inches long and  $\frac{1}{2}$ -inch bore, were closed at one end and each frequently filled and agitated with a different water during various periods. One water with a total hardness of  $3.5^\circ$  and a permanent hardness of  $3.2^\circ$ , dissolved considerably more lead than another with a total hardness of  $18.6^\circ$  and permanent hardness of  $5^\circ$ ; a relationship that was not altered by charging both with carbonic anhydride. But the activity of the first was destroyed by thoroughly agitating with precipitated calcium carbonate and filtering. D. A. L.

**Cause of the Retention and Release of Gases Occluded by Metallic Oxides.** By THEODORE W. RICHARDS (*Amer. Chem. J.*, 1898, 20, 701—732).—Scott has recently stated (*Trans.*, 1897, 559) that copper oxide prepared by exposing the nitrate to a "full red heat" in a muffle-furnace, contains only one-tenth the volume of occluded gas previously found by the author to be present in ignited copper oxide (*Abstr.*, 1891, 805); the statement is, however, not a

contradiction of the latter's results, since these were obtained at much lower temperatures, in most cases not exceeding  $700^{\circ}$ . Experiments are now described which confirm the conclusions formerly arrived at: that copper oxide prepared by the ignition of the nitrate by Hampe's method, contains between 4—5 times its volume of occluded gas, and that the latter is partially expelled at a red heat. Nearly the whole of the gas is retained until the temperature rises above  $850^{\circ}$ , when nine-tenths of it is rapidly evolved; at higher temperatures, the oxide is partially decomposed, with loss of oxygen. The amount of gas retained by the oxide below  $850^{\circ}$  does not depend on the time of ignition, although it is dependent on it above this temperature.

When zinc oxide, prepared by heating the pure nitrate during a long period at  $280^{\circ}$ , is ignited at temperatures between  $660^{\circ}$  and  $880^{\circ}$ , the amount of gas retained diminishes as the temperature rises, other conditions being the same; continued heating at one temperature causes a slow evolution of the gas. The total amount of gas occluded by zinc oxide varies greatly according to the method used for preparing the latter, and according to its physical condition. Whilst the actual amount of nitrogen occluded by the same specimen of zinc oxide is independent of the temperature at which it is subsequently ignited, the quantity of oxygen retained decreases as the temperature is increased. Richards and Rogers' results (*Abstr.*, 1894, ii, 45) are thus confirmed, whilst Morse and Arbuckle's statement to the contrary (*Abstr.*, 1897, ii, 334) is shown to be incorrect. In the case of copper oxide, the more rapid evolution of occluded oxygen at high temperatures is still more marked, but it is not so evident in the case of magnesium oxide.

From his results, the author concludes that the occluded gas is due to a residue of basic nitrate imprisoned in the oxides in question; that the oxygen escapes more rapidly than the nitrogen when this residue is decomposed, is explained by assuming that the loss takes place, not by diffusion, but by chemical transference. According to this hypothesis, the particles of copper oxide in immediate contact with the imprisoned gases dissociate into copper and oxygen, and then remove a portion of the occluded oxygen by combining with it; the oxygen is subsequently transferred from molecule to molecule by changes similar to those assumed to take place by Clausius's theory of electrolysis, until it finally escapes. This view is supported by the fact that the occluded oxygen is lost much more rapidly by copper oxide than by the oxides of zinc and magnesium, which are far less easily dissociated. That metallic copper is liberated when copper oxide is ignited at a red heat is shown by a great increase in the latter's conductivity; under the same conditions, the conductivity of zinc oxide was much less changed, whilst that of magnesium oxide remained unaffected. It also appears that when copper oxide is heated in a vacuum at  $790^{\circ}$ , oxygen is evolved as long as it is rapidly removed, cuprous oxide being formed. The apparent volatility of cadmium oxide at high temperatures is probably due to its initially dissociating into oxygen and cadmium, which sublimes and is then reoxidised.

W. A. D.

**Action of Hydrogen Phosphide on Cupric Sulphate.** By E. RUBÉNOVITCH (*Compt. rend.*, 1898, 127, 270—273).—When hydrogen phosphide is allowed to act on cupric sulphate solution without any special precautions, the composition of the product is complex and variable, but if the pure gas, prepared from phosphonium chloride, is allowed to act on the copper salt in complete absence of oxygen, a black product is obtained which consists solely of the phosphide  $P_2Cu_5 + H_2O$ . One-third of the phosphorus in the hydrogen phosphide is converted into phosphoric acid, and the acid of the cupric salt is found in the free state in the liquid  $10CuSO_4 + 5Ph_3 + 6H_2O = 2(P_2Cu_5 + H_2O) + H_3PO_4 + 10H_2SO_4$ . The changes in the colour of the solution indicate that part of the cupric salt is first reduced to cuprous salt.

The black phosphide begins to lose water at  $80^\circ$  and is completely dehydrated at  $150^\circ$ , the colour changing to red-brown. It oxidises much more readily when anhydrous than when hydrated; in contact with the liquid in which it was formed, it is readily oxidised by air with liberation of metallic copper and formation of more phosphoric acid. Nitric acid and bromine attack the phosphide readily; potassium permanganate oxidises it, and concentrated sulphuric acid dissolves it with liberation of hydrogen phosphide. C. H. B.

**Aluminium as a Reducing Agent.** By LÉON FRANCK (*Chem. Zeit.*, 1898, 22, 236—245).—When aluminium in a finely divided state is heated to redness in an atmosphere of hydrogen and phosphorus vapour, a vigorous reaction takes place, and a dark-grey, infusible phosphide is produced having the composition  $Al_3P_7$ . An intimate mixture of aluminium and phosphorus, heated to white heat in a current of hydrogen, yields another phosphide,  $Al_3P_3$ , which forms a yellowish-grey, infusible mass. Dark blue, shining needles are obtained in small quantity by heating aluminium and phosphorus in sealed tubes, but their exact composition has not been determined. Two other phosphides,  $Al_3P$  and  $Al_2P_2$ , which have a metallic appearance and a crystalline fracture, are obtained by the use of the electric furnace. All the above phosphides give off phosphine when treated with water or acids.

A mixture of aluminium and sodium metaphosphate, when heated to redness in a current of hydrogen, yields half the phosphorus in the free state, whilst half remains combined with the metal, forming  $Al_5P_3$ ; if silica be added to the mixture, the whole of the phosphorus is liberated. Calcium phosphate behaves in a similar manner, but calcium metaphosphate containing calcium sulphate cannot be employed in this experiment, as the presence of the latter salt causes explosions when the mixture is heated.

Aluminium, like magnesium, decomposes carbonic anhydride and carbonic oxide, forming the oxide of the metal and free carbon. A mixture of the metal and lampblack, when heated to a white heat, gives rise to a certain amount of aluminium carbide, which, however, cannot be separated from the excess of carbon.

The carbonates of lithium, sodium, potassium, calcium, strontium,

and barium are reduced on heating with aluminium, the products being alumina, carbon, and the free elements; the latter alloy with the excess of aluminium, and in all cases a small amount of aluminium carbide is formed.

Aluminium reduces the metallic oxides when heated with them to sufficiently high temperatures; in the case of the oxides of silver, copper, and lead, the reaction proceeds with explosive violence. The oxides of iron, manganese, cobalt, nickel, chromium, and molybdenum are all partially reduced; boron and silicon are easily obtained from their oxides.

A mixture of powdered aluminium and sodium peroxide, when moistened with water, ignites spontaneously. G. T. M.

**Formation of Alums by Electrolysis.** By J. LEWIS HOWE and E. A. O'NEAL (*J. Amer. Chem. Soc.*, 1898, 20, 759—765).—The preparation of manganese alums, the primary object of the research, was not effected; various alums were, however, prepared by passing currents of 0.02—0.19 ampères through solutions of sulphates of the metals together with excess of sulphuric acid. The anode consisted of a platinum dish or crucible, and the cathode, which was immersed in a porous cup, of a platinum wire.

Iron ammonium alum was prepared by passing the current through a solution of the sulphates of ammonium and iron acidified with sulphuric acid; the alum is formed at the anode. In a similar manner, iron potassium alum, iron rubidium and iron caesium alums, cobalt rubidium and cobalt caesium alums were prepared.

Chromium ammonium alum was formed when the cathode dipped into a solution of ammonium chromate acidified with sulphuric acid. With manganese sulphate and the sulphates of ammonium, rubidium, and caesium, no satisfactory results could be obtained, although Piccini has just stated that he obtained caesium manganese alum by electrolytic oxidation (*Abstr.*, 1898, ii, 521). From solutions containing ruthenium, no alum was obtained, but it was observed that ruthenium tetroxide was evolved at the positive pole. G. W. F. H.

**Action of Water and Saline Solutions on Metallic Iron.** By ROBERT MELDRUM (*Chem. News*, 1898, 78, 202—203).—Numerous experiments have led the author to the conclusion that the oxidation of iron in water takes place in the absence of ammonia, carbonic anhydride, or of bacteria and other forms of life, but it is uncertain whether the action is due to the water itself or to dissolved oxygen. The experiments were made with piano wire, in glass bottles free from lead, in the light; generally, a white cloud formed immediately round the metal, which extended and in 15 minutes the whole liquid became cloudy and then yellow; a yellow precipitate forming in 3 or 4 hours. Sometimes the internal surface of the glass was coated with an iridescent film, from which glistening plates became detached, and were found in the precipitate of hydrated oxides; this occurred when the surface of the iron exposed was great in proportion to the volume of water, and when there was free contact with the air. In bottles half full of solutions of pure salts, activity was observed in the following cases, the solutions employed being of 1 per cent.

strength—ammonia, sodium carbonate, sodium hydrogen carbonate, sodium hydrogen phosphate, potassium hydrogen phosphate, sodium metaphosphate, sodium pyrophosphate, and potassium borate, whilst sodium baborate and potassium baborate gave white precipitates. The following do not show any action : calcium hydroxide (saturated solution), sodium peroxide, sodium hydroxide, potassium hydroxide, barium hydroxide, strontium hydroxide (5 per cent. solution). The experiments extended, in some cases, to 4 weeks. It seems that alkaline potassium salts are more active than the corresponding sodium salts.

D. A. L.

**A Double Iron Tungsten Carbide.** By P. WILLIAMS (*Compt. rend.*, 1898, 127, 410—412).—On heating a mixture of tungstic anhydride, 150 grams; iron, 250 grams, and petroleum coke, 80 grams, in a carbon crucible in an electric furnace with an arc from a current of 900 ampères and 45 volts, an iron tungsten carbide, most probably  $2\text{Fe}_3\text{C}, 3\text{W}_2\text{C}$ , is obtained. The product is treated two or three times with hot concentrated hydrochloric acid, and the double carbide, which is highly magnetic, is separated by means of a magnet. It is then treated with aqua regia, which dissolves about half the crystals and leaves a residue of definite composition.

The double carbide thus obtained forms very brilliant, microscopic prisms with the colour of pyrites; it scratches glass easily, but not rock crystal; sp. gr. = 13.4 at 18°. At a red heat, it is not affected by hydrogen or by hydrogen sulphide, but is attacked by chlorine, bromine, iodine, and oxygen; it is not affected by water vapour at the softening point of glass, but oxidises slowly in moist air. Gaseous hydracids have no action, but their solutions decompose the carbide in sealed tubes at about 250°; nitric and sulphuric acids dissolve it rapidly, and it is also decomposed by alkalis and by oxidising agents.

C. H. B.

**Tungsten Silicide.** By ÉMILE VIGOUROUX (*Compt. rend.*, 1898, 127, 393—395).—*Tungsten silicide*,  $\text{W}_2\text{Si}_3$ , forms beautiful, steel-gray plates with a metallic lustre; sp. gr. = 10.9. It is attacked by chlorine, with incandescence between 200° and 300°; by bromine, without incandescence, below a red heat, and by iodine, without incandescence, above a red heat. In oxygen, it burns very brilliantly at about 500°, and in air it oxidises below a red heat, but does not burn; nitrogen is without action at any temperature. The ordinary acids, including hydrofluoric, have no action even on heating. Aqua regia is practically without action, but a mixture of nitric and hydrofluoric acids attacks the silicide violently, even at the ordinary temperature. Alkalis in solution have little action, but fused alkali hydroxides and carbonates decompose the silicide very readily, whilst fused potassium nitrate acts with somewhat less energy.

Tungsten silicide is prepared by heating in the electric furnace a mixture of 100 grams of silicon with 230 grams of tungsten oxide obtained by heating ammonium tungstate. The heavy, brittle, crystalline product is suspended in dilute hydrochloric acid (1 in 10), and connected with the positive pole of a battery of two or three cells, a carbon plate placed in the liquid being connected with the negative

pole. The metal dissolves, and the silicide, which collects at the bottom of the vessel, is treated successively with aqua regia, ammonia, and hydrofluoric acid, and any carbon silicide that may be present is separated by means of methylenic iodide.

C. H. B.

**Extraction of Thorium on a large Scale.** By GRÉGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Compt. rend.*, 1898, 127, 412—414).—The mineral is dissolved in the usual way, and the solution, which must contain sufficient acid to prevent precipitation of the phosphates, is precipitated with half the quantity of oxalic acid necessary for complete precipitation. The oxalates are washed until free from phosphoric acid, converted into carbonates by means of a hot solution of sodium carbonate (1:10), and some sodium hydroxide added to insure complete precipitation of the thorium. The carbonates are washed until free from oxalic acid, dissolved in just the necessary quantity of hydrochloric acid, and mixed with successive small quantities of barium peroxide suspended in water until the liquid gives no precipitate with hydrogen peroxide. The precipitated peroxide contains all the thorium, together with 20 to 30 per cent. of impurities; it is washed and dissolved in cold concentrated hydrochloric acid, barium eliminated by means of sulphuric acid, enough water added to yield a solution containing 15 per cent. of acid, and the bases precipitated with oxalic acid. The oxalates are washed, and treated with a highly concentrated solution of ammonium carbonate mixed with sufficient ammonia to form the normal salt. By two or three successive treatments, all the thorium is dissolved, and the solution is precipitated by means of sodium hydroxide, the precipitate well washed and dissolved in not more than the requisite quantity of nitric acid, and the liquid poured into sufficient water to yield a solution containing not more than 2 per cent. of thorium. Excess of hydrogen peroxide is then added, and the precipitate is well washed.

From this point, all the reagents must be pure. The precipitate is dissolved in nitric acid and reprecipitated with hydrogen peroxide in order to eliminate all the cerium. It is next dissolved in hydrochloric acid, precipitated with oxalic acid, and the oxalate decomposed by pure sodium hydroxide. After careful washing, the precipitate is again dissolved in hydrochloric acid and precipitated with ammonia. This final precipitate is well washed, dissolved in nitric acid, and the nitrate crystallised.

In treating 5 tonnes of monazite, the authors never obtained, either in the hydrogen peroxide precipitate or in the ammonium carbonate solution of the oxalates, any element corresponding with the *Russium* of Chrutchoff.

C. H. B.

**Electrolytic Gold Refining.** By EMIL WOHLWILL (*Zeit. Elektrochem.*, 1898, 4, 379, 402, and 421).—Solutions in potassium cyanide cannot be used, because silver and copper are deposited along with the gold. When neutral solutions of auric chloride or of hydrogen aurichloride,  $\text{HAuCl}_4$ , are used, chlorine is evolved and the gold anode is not attacked. With hydrochloric acid alone, even so dilute as 0.4 gram per litre, or with solutions of hydrogen aurichloride acidified with hydrochloric acid, no chlorine is evolved, and the gold is dissolved;

the chlorides of the alkalis or of ammonium have the same effect as hydrochloric acid. In order that the gold anode shall dissolve, it is, therefore, necessary that the conditions permit of the formation of  $\text{AuCl}_4$  ions. The behaviour of gold chloride solutions towards silver nitrate confirms Hittorf's conclusion as to the existence of these ions; reddish-yellow precipitates are invariably formed on adding the silver nitrate; they are, however, much less stable than the analogous silver platinochloride. The dissolution of the anode is also promoted by raising the temperature to  $60^\circ$  or  $70^\circ$ , and in a hot solution containing about 3 per cent. of hydrochloric acid, an anodic current density of 3000 ampères per square metre may be employed without separation of free chlorine; this is more than sufficient for practical purposes. At the cathode, a fairly high current density may be employed without injury to the gold deposit, and without necessitating the use of too concentrated a gold solution; the deposit is usually coarsely crystalline, and sufficiently adherent to permit of thorough washing without loss. The greater the concentration of the gold solution, the better the deposit; 30 grams of gold per litre is, however, sufficient, even with 3000 ampères per square metre. No trouble is experienced from the formation of dendritic deposits, so that the electrodes may be placed close together, and a considerable output be obtained from a small plant.

Of the impurities in the gold, platinum and palladium pass into solution, but are not deposited at the cathode; after they have accumulated sufficiently, the solutions are worked up to recover them. Silver remains, mainly as a mud of silver chloride; the small part which dissolves in the hot acid solution does not pass into the deposited gold. The refined gold is very seldom less than 999.8 fine, not infrequently it is 1000. The E.M.F. required with a current density of 1000 ampères per square metre is less than 1 volt.

On the assumption that only tervalent gold exists in the solution, 2.45 grams should be deposited per ampère hour. The author's experiments, as well as the results obtained in large scale working, show that more nearly 3 grams per ampère hour are obtained. A consideration of the loss of gold at the anode gives the explanation of this. Part of the loss is due to the separation of fine particles of gold which are found, for the most part, in the silver chloride mud. These particles are equal to about one-tenth of the amount of gold deposited on the cathode, and are not merely mechanically detached from the anode, but are due to the formation of aurous chloride at its surface, which subsequently decomposes into metallic gold and auric chloride. In support of this view, the author shows that the particles are much purer than the anode itself; that aurous chloride may be detected in the solution, and that, under certain circumstances, small crystals of gold separate out throughout the mass of the solution. The presence of aurous gold with three times the electro-chemical equivalent of the auric gold readily accounts for the large deposit observed. The part of the gold dissolved from the anode in the aurous state, which decomposes into metallic gold and auric chloride, never reaches the cathode, and, therefore, the loss at the anode is always greater than the deposit at the cathode. A series of experiments with varying anodic current



densities shows that the formation of univalent gold ions diminishes as the current density increases. With 1500 ampères per square metre, 2.48 grams of gold per ampère hour were deposited (instead of 2.45), and the loss at the anode and gain at the cathode, in two experiments, were (1) 105.2 : 104.5 ; (2) 107.7 : 105. Here, therefore, tervalent gold was present almost exclusively. Such results are only obtained when the liquid is well stirred ; otherwise, owing to the accumulation and decomposition of aurous chloride at the anode, the loss there is much in excess of the cathode gain. In experiments with very small current densities, the non-electrolytic solution of gold in the hot, acid auric chloride solution must be allowed for. This appears to be reversible, a sheet of gold losing weight when the temperature is raised, and gaining it when it is lowered again. After allowing for this chemical attack, the author obtained with 1 ampère per square metre a deposit of 4.33 grams per ampère hour, and an anodic loss of 6.01 grams, that is, 72.5 per cent. of the gold had dissolved in the aurous state.

T. E.

**Claims of Davyium to Recognition as an Element.** By JOHN W. MALLET (*Amer. Chem. J.*, 1898, 20, 776—783).—Kern (this Journal, 1877, ii, 278 and 712) has stated that platinum ores contain a small quantity of a new metal, "davyum," characterised by its chloride combining with that of sodium to form a sparingly soluble double salt. In the hope of separating this metal, the author has examined the sparingly soluble residue remaining after clearing a solution of platinum ore in aqua regia from osmiridium by decantation, removing the platinum by adding ammonium chloride, adding an excess of common salt, evaporating to dryness, and extracting the residue with a minimum of water. It was found, however, to consist only of quartz, zircon, iridium, rhodium, and osmium.

From a large quantity of rose-coloured crystals of sodium chloride recovered during the manufacture of platinum, a very small amount of a metallic substance was isolated, which, judging from an analysis of the double chloride, appeared to have an atomic weight of about 151.5, corresponding with the value 154 attributed by Kern to davyum. Its solution also in aqua regia gave a red coloration with potassium thiocyanate, a reaction characteristic of davyum. Since, however, it was found to consist merely of rhodium and iridium with a trace of iron, the existence of davyum is considered as very doubtful.

W. A. D.

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### Mineralogical Chemistry.

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Origin of the Freiberg Mineral Veins. By ALFRED W. STELZNER (*Zeit. prakt. Geol.*, 1896, 377—412).—Sandberger has found the mica from the gneisses carrying the Freiberg lead veins to contain small quantities of heavy metals, and on this he founded his theory of lateral secretion to explain the origin of mineral veins. The

present author gives the results of numerous analyses made on large quantities of fresh mica from the Freiberg gneiss and from the gneisses and granites of the Black Forest, but these do not confirm Sandberger's results. None of these micas show the presence of heavy metals (lead, silver, &c.) other than small quantities of cobalt, nickel, copper, and zinc, and since sulphur was also found these probably exist as sulphides mechanically enclosed in the mica, rather than as silicates entering into the constitution of the mica, as was supposed to be the case by Sandberger. Several other arguments are brought against the theory of lateral secretion. The material of the veins has more probably been brought up from great depths by mineral waters, and only a small amount leached out of the rocks surrounding the veins.

L. J. S.

**Copper, Bornite, and Petalite from the Caucasus.** By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1898, 30, 388; from *Verh. kais. russ. min. Ges.*, 1896, 34, 55).—Distorted crystals of native copper and cubes of erubescite (= bornite) with convex faces are described. Petalite from the Amana glacier, Batalpaschinsk district, gave, on analysis by J. A. Antipow,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MnO.	Na <sub>2</sub> O, K <sub>2</sub> O.	Li <sub>2</sub> O.	Loss on ignition.
77.28	14.82	1.08	0.58	trace	2.07	1.97	0.45

L. J. S.

**Diaphorite from Washington and Mexico.** By LEONARD J. SPENCER (*Amer. J. Sci.*, 1898, [iv], 6, 316).—Orthorhombic crystals of the rare mineral diaphorite are noted from two new localities: (1) Lake Chelan district, Okanogan Co., Washington; associated with stephanite and pyrargyrite; (2) Santa Maria de Catorce, San Luis Potosi, Mexico; with miargyrite.

The three minerals, andorite (Abstr., 1898, ii, 120), diaphorite, and freieslebenite, are strikingly similar in appearance, and between them there is the same kind of morphotropic relation as that which exists between the members of the humite group (Abstr., 1894, ii, 241).

	<i>a</i>	<i>b</i>	<i>c</i>	Sp. gr.	Chem. comp.
Andorite.....	0.9846	: 1	: 0.6584	5.35	(Pb, Ag <sub>2</sub> )S, Sb <sub>2</sub> S <sub>3</sub>
Diaphorite .....	0.9839	: 1	: 0.7345	5.9	5(Pb, Ag <sub>2</sub> )S, 2Sb <sub>2</sub> S <sub>3</sub>
Freieslebenite ...	0.9786	: 1	: 0.9277	6.3	5(Pb, Ag <sub>2</sub> )S, 2Sb <sub>2</sub> S <sub>3</sub>

 $\beta = 87^\circ 46'$ .

Since, in diaphorite, the vertical axis *c* and the sp. gr. fall between those of andorite and freieslebenite, it is to be expected that it should also be intermediate in composition. Brongniardite, which has such an intermediate formula, namely, 2(Pb, Ag<sub>2</sub>)S, Sb<sub>2</sub>S<sub>3</sub>, agrees in sp. gr. and external characters with diaphorite; it therefore seems very probable that brongniardite and diaphorite are identical. (The so-called cubic crystals of brongniardite are identical with stanniferous argyrodite, Abstr., 1898, ii, 436.)

L. J. S.

**Cubanite from Butte, Montana.** By HORACE V. WINCHELL (*American Geologist*, 1898, 22, 245).—A brass-yellow mineral, now being mined as a copper ore at Butte, gave, on analysis by S. J. Gormly,

Cu.	Fe.	S.	SiO <sub>2</sub> .	Ag.	An.
25.04	34.26	39.90	0.77	0.96 oz.	trace

Other determinations of the copper gave 25.35, 19.8, and 23.6 per cent. The excess of copper over that required by the cubanite formula,  $\text{CuFe}_2\text{S}_4$ , is probably due to the presence of bornite.

L. J. S.

**Lonchidite from Olkusch.** By J. A. ANTIPOV (*Zeit. Kryst. Min.*, 1898, 30, 388; from *Verh. kais. russ. min. Ges.*, 1896, 34, 24).—A spheroidal concretion of marcasite with fibrous structure was found to contain As, 5; Te, 0.3 per cent.

L. J. S.

**Nickeliferous Magnetites.** By WILLET G. MILLER (*Rept. Brit. Assoc.*, 1898 [for 1897], 67, 660—661).—Samples of ore from the larger deposits of titaniferous magnetite in eastern Ontario have been found to contain nickel (and cobalt) to the extent of 0.8 per cent. No nickel has been found in the non-titaniferous magnetites of the district. The former are considered to be of igneous origin, and the latter of aqueous or mechanical origin. The high quality of iron extracted from the titaniferous ores may be due to the presence of nickel.

L. J. S.

**Interaction of Calcium Hydrogen Carbonate and Alkali Sulphate: Formation of Alkali Carbonates in Nature.** By HEINRICH VATER (*Zeit. Kryst. Min.*, 1898, 30, 373—386).—Hilgard and Tanatar have determined the amount of alkali carbonate which, with gypsum, is formed when carbonic anhydride is passed through a solution of alkali sulphate in contact with an excess of calcium carbonate, and they have explained the natural formation of alkali carbonates by this reaction (*Abstr.*, 1893, ii, 165; 1896, ii, 419; 1897, ii, 58). The present author adversely criticises these results, and considers that alkali carbonates in the solid form cannot be obtained in this manner. The alkaline reaction of the solution he attributes to calcium carbonate. From solutions not in contact with solid calcium carbonate, there is a separation of calcium carbonate or of the double salt,  $\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ , but not of gypsum or alkali carbonate.

L. J. S.

**Alkaline Reaction of some Natural Silicates.** By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1898, 20, 739—742).—The author describes experiments on the decomposing action of pure water on various natural silicates. For this purpose, the finely-powdered mineral was shaken with water to which a minute quantity of phenolphthalein had been added, the alkalinity of the water, as measured by the depth of colour imparted to it in the presence of the phenolphthalein, being taken as a measure of the susceptibility to decomposition by water of the mineral in question.

Amongst the micas, muscovite and lepidolite are only very slightly affected by water, whereas phlogopite, a magnesium mica, is readily attacked; similarly, orthoclase is but slightly acted on, oligoclase more readily, albite still more readily. These observations are in accord with the observed susceptibility to weathering of the minerals in question.

Leucite, nephelite, spodumene, scapolite, laumontite, stilbite, chabazite, and thomsonite gave very little coloration; heulandite and analcite stronger colorations; cancrinite, sodalite, natrolite, pectolite, apophyllite, agirite still stronger colorations. G. W. F. H.

[Baddeckite, Tennantite, &c., from Canada.] By G. CHRISTIAN HOFFMANN (*Ann. Rept. [1896], Geol. Survey Canada, 1898, 9, R. 1—53*).—The name baddeckite is given to a micaceous mineral occurring as minute scales and scaly aggregations in clay at Baddeck, Victoria Co., Nova Scotia. It is copper-red and gives a tile-red streak; before the blowpipe, it fuses to a black, magnetic glass, and it is decomposed by strong hydrochloric acid, with separation of gelatinous silica. Analysis by R. A. A. Johnston gave,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
48·96	13·85	25·82	1·17	2·65	3·47	0·22	3·78	99·92	3·252

Formula,  $2\text{H}_2\text{O}(\text{Ca}, \text{Mg}, \text{K}_2, \text{Na}_2)\text{O} \cdot 3(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 8\text{SiO}_2$ . The mineral is, therefore, considered to be a variety of muscovite (hydromuscovite) with alumina largely replaced by ferric oxide. (Also in *Amer. J. Sci.*, 1898, 6, 274).

Tennantite occurs near the Bonaparte River, Lillooet district, British Columbia; it is usually massive, but rarely in tetrahedra. Colour, dark greyish-black; thin splinters are translucent and deep ruby-red by transmitted light; streak, cherry-red. It contains 41·51 Cu and 0·2385 Ag per cent.; besides much arsenic and sulphur, there are also small quantities of Sb, Pb, Zn, and Fe. Chalcantite, in fine specimens, results from the alteration of this tennantite.

A straw-yellow, crystalline incrustation on limestone in the Alberta district, North-west Territory, is readily soluble in water, and gave on analysis by Johnston,

SO <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	MgO.	H <sub>2</sub> O.	Insol.	Total.
36·43	13·15	0·93	5·57	5·92	36·98	0·48	99·46

This corresponds with a mixture of epsomite and a hydrated basic ferric sulphate, possibly fibroferriite.

Xenotime, in masses weighing up to 312 grams, occurs in a granite vein at Calvin, Ontario; sp. gr. = 4·395.

The report also includes various other mineralogical notes (with partial analyses and sp. gr. determinations), also analyses of coals, rocks, waters, nickel and cobalt ores, and the results of numerous gold and silver assays. L. J. S.

**Kaolinite Deposits of South Russia.** By PETR A. ZEMJAT-SCHENSKY (*Zeits. Kryst. Min.*, 1898, 30, 389; from *Trav. Soc. Naturalistes, St. Petersbourg*, 1896, 1—322).—Kaolinite from various Russian localities is described from geological and chemical points of view. The following formulæ are given.  $2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$  ( $= \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ );  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ;  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ ;  $2\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$  ( $= \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ );  $\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ;  $3\text{Al}_2\text{O}_3 \cdot 20\text{SiO}_2$ ;  $8\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2$ . Water begins to be given off at 300°; between 300—400°, a small portion is expelled, and complete dehydration is effected at 700—770°. Kaolinite has an acid character, in that the hydrogen, or a part of it, is easily replaced by a

metal. With haloid compounds of the alkalis, it gives a product allied to muscovite, and with sulphur compounds it gives hydrogen sulphide. With ferrous sulphate at a high temperature and pressure, sillimanite, or a product resembling chlorite, is formed. L. J. S.

Norites [Hypersthene, Diallage, Enstatite, and Anorthoclase] from the Transvaal. By J. A. LEO HENDERSON (*Inaug.-diss. Leipzig* (London), 1898, pp. 1—56).—The following analyses by Röhrig are given of minerals separated by heavy liquids from some of the South African rocks described in this thesis. Diallage-norite (sp. gr. = 3·01) from the Zwaartkoppies range is composed of basic plagioclase (sp. gr. = 2·7), hypersthene, diallage, and a colourless to pale-green pyroxene resembling salite. The hypersthene (anal. I) is strongly pleochroic, and the diallage (II), with extinction angle 46°, contains numerous acicular enclosures, possibly of rutile; the hypersthene and diallage form very intimate regular intergrowths, and it was not possible to obtain absolutely pure material for analysis. The analyses give the formula  $R''O, SiO_2$ , with some  $MgO, (Fe, Al)_2O_3, 4SiO_2$ . Hypersthene, in a similar rock (sp. gr. = 2·87) from the same locality, gave III. Hypersthene-norite (sp. gr. = 2·93), from the Hex River near Rustenburg, consists of plagioclase (sp. gr. = 2·71) and pleochroic hypersthene (IV); the latter encloses numerous small, colourless plates, probably of plagioclase, arranged parallel to the pinacoid faces. A finely crystalline quartz-norite (sp. gr. = 2·97), from the Marico district, is composed of felspar, hypersthene, diallage, quartz, and biotite; the hypersthene (V, also alkalis 2·17;  $MnO$ , 0·67 per cent., and  $Cr_2O_3$ , trace) is only very slightly pleochroic, and the material analysed enclosed plates of biotite arranged parallel to the pinacoid faces. The quartz in this rock forms micropegmatitic intergrowths with the felspar. These norites, which have been previously described as gabbros, contain no olivine. An enstatite-pyroxenite, from the Marico district, composed entirely of granules of green enstatite, gave anal. VI. The enstatite, however, encloses numerous minute plates of anorthite, as shown by the analysis, to the extent of 4·5 per cent.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	51·64	0·34	1·32	4·41	18·62	14·74	6·46	1·50	99·03	3·50
II.	52·54	0·21	0·24	5·12	12·46	12·02	17·12	—	99·71	3·36
III.	54·49	—	trace	21·84		19·21	4·40	—	99·94	3·38
IV.	50·28	0·24	1·49	9·79	7·82	23·00	7·33	0·16	100·11	3·36
V.	53·35	0·36	4·50	5·12	13·32	16·15	4·42	0·40	100·46	3·366
VI.	55·23	0·44	2·08	3·94	6·25	29·29	1·68	1·12	100·03	3·297

Amphibole-pyroxene-syenite (hatherlite), from Hatherley near Pretoria, is composed of anorthoclase, hornblende, pyroxene, and biotite, with very little quartz. The large anorthoclase crystals have an angle of optical extinction on  $c(001)$  of 9—12°; they consist of a core of white felspar (anal. VII) surrounded by a zone of red felspar (VIII). Large porphyritic crystals of dark-red anorthoclase in porphyry (pilandite) from the Pilandsberge gave IX; the ground-mass of this rock consists of red felspar and amphibole, with very little quartz. From these analyses, small quantities of  $Fe_2O_3$ ,  $MgO$ , and  $H_2O$  have been eliminated. These rocks, to which the new names hatherlite and

pilandite are given, are considered to be the plutonic and porphyritic equivalents respectively of the volcanic anorthoclase-bearing rock pantellarite.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.	Sp. gr.
VII.	61·81	24·68	2·71	7·53	3·37	100·10	2·65
VIII.	64·06	21·68	1·87	7·53	4·50	99·64	2·56
IX.	66·31	20·60	0·48	7·54	4·92	99·85	2·60

L. J. S.

**Origin, Composition, and Alteration of Glaucconite.** By KONSTANTIN D. GLINKA (*Zeit. Kryst. Min.*, 1898, 30, 390—391; St. Petersburg, 1896, pp. 114. Compare Abstr., 1896, ii, 568; 1897, ii, 54).—Ten analyses are given of glaucconite isolated from Russian sandstones, and one limestone; the extreme amounts of each constituent are quoted below. The dark-green grains have sp. gr. = 2·7—2·8, and the yellowish green 2·4—2·5.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O at 100°.	H <sub>2</sub> O on ignition.	Sp. gr.
41·02	5·84	8·17	1·32	—	0·69	5·74	0·30	2·42	4·45	2·400
52·96	22·19	23·43	5·95	8·37	4·11	9·54	0·98	7·79	7·88	2·867

Glaucconite and celadonite, when heated with potassium carbonate solution, take up potassium; solutions of various chlorides have no action.

L. J. S.

**Granitic Rocks of the Riesengebirge.** By LUDWIG MILCH (*Jarhb. f. Min.*, 1898, Beil. Bd. 12, 115—237).—In this petrographical paper, the following analyses of biotite are given by W. Herz. I. Biotite from biotite-granite of the Schneekoppe; the rock itself gave anal. III. II. Biotite from a basic streak in biotite-granite from Arnsdorf; the streak gave anal. IV., and the biotite-granite gave V. Twenty-one other rock analyses are given.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	40·38	15·40	5·26	7·73	—	19·87	7·11	1·80	1·68	99·23
II.	39·66	14·26	4·01	8·10	—	20·48	7·99	2·60	2·04	99·14
III.	72·81	15·22	1·88	1·40	2·77	1·10	1·54	2·10	1·66	100·48
IV.	63·06	18·01	2·48	1·91	2·72	4·55	3·88	2·01	2·20	100·22
V.	74·65	12·64	2·26	0·85	2·12	1·01	2·37	3·41	1·14	100·45

L. J. S.

**Dunite in Massachusetts.** By G. C. MARTIN (*Amer. J. Sci.*, 1898, [iv], 6, 244—248).—A boss of dunite is intrusive into the gneisses near Chester, in the Green Mountain region of western Massachusetts. It is in part altered to serpentine. The pale green olivine isolated from the altered rock gave, on analysis,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.
40·07	1·94	4·84	51·41	—	1·03	99·29	3·27

L. J. S.

**Vanadium and Molybdenum in Rocks of the United States.** By WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1898, [iv], 6, 209—216; and *Chem. News*, 1898, 78, 216—219).—Vanadium has long been known to occur in small quantities in various rocks and minerals. Quantitative determinations of the vanadium present in 64 rocks

from the United States show that it occurs in appreciable amounts in the more basic igneous and metamorphic rocks (up to 0.08 per cent. of  $V_2O_3$ ), but that it is absent, or nearly so, in the highly siliceous rocks. The existence of the vanadium mica, roscoelite, suggests that this element is present as  $V_2O_3$  rather than as  $V_2O_5$ , and that it occurs in the heavier aluminous silicates biotite, pyroxene, and amphibole. Determinations of the amount of vanadium in these minerals are given; for example, in biotite (0.127 per cent.  $V_2O_3$ ), isolated from pyroxenic gneiss (0.083,  $V_2O_3$ ) from Calaveras Co., California; amphibole (0.037,  $V_2O_3$ ) from Californian amphibole-gabbro (0.02,  $V_2O_3$ ).

Molybdenum was found in only a few of the rocks, and then only as traces in the more acid ones.

Full details are given of the methods and precautions used in the analyses. The determinations were made on 5 grams of material.

L. J. S.

**Meteoric Iron from Beaconsfield.** By EMIL W. COHEN (*Sitz.-ber. Akad. Berlin*, 1898, 306—307. Compare Abstr., 1898, ii, 171).—In the previous description of this iron, it was stated that carbon having the appearance of anthracite was present; this was found after dissolving the meteoric iron in dilute hydrochloric acid, and treating the residue with cupric ammonium chloride in order to separate the tænite and cohenite from the schreibersite and rhabdite. It is now found that this anthracitic carbon is not an original constituent of the iron, but is formed by the action of the cupric ammonium chloride on the cohenite. Although cohenite,  $Fe_3C$ , contains only about  $6\frac{1}{2}$  per cent. of carbon, this carbonaceous residue is compact and shining. The crystals of cohenite from the Toluca and Beaconsfield irons give homogeneous solid pieces, whilst the crystalline aggregates of cohenite from the Niakornak iron give finely granular carbon possessing little cohesion.

It is suggested that some anthracites, for example that of mineral veins, may have been formed by the alteration of carbides, which are now known to be of terrestrial origin (Abstr., 1898, ii, 83, 232).

L. J. S.

**Meteoric Iron from San Cristobal, Chili.** By EMIL W. COHEN (*Sitz.-ber. Akad. Berlin*, 1898, 607—608).—Four fragments of this iron were brought to Europe in 1896 from the San Cristobal gold-mining district near Antofagasta in Chili; one of the fragments weighs 60 grams. Troilite nodules are surrounded by a zone of schreibersite, and this again by a zone of dark nickel-iron. The main mass of the iron shows an intricate structure on the surface; this appears to be due to minute lamellæ, which are much bent and twisted. Putting aside the Oktibbeha Co. and Santa Catharina irons as being doubtfully meteoric, this iron differs from all other meteorites in the high percentage of nickel and in its peculiar structure; it is, therefore, placed in a special class of the ataxites. Analysis by O. Sjöström gave

Fe.	Ni.	Co.	P.	Total.	Sp. gr.
73.72	25.60	1.00	0.18	100.50	7.8593

L. J. S.



**Mineral Water from Selters, Nassau.** By HEINRICH FRESSENIUS (*Jahrb. Nassau Ver. Naturk.*, 1898, 51, 1—23).—Water from a new boring at Selters, near Weilburg, on the Lahn, is clear and has a temperature of  $13^{\circ}$ ; sp. gr. = 1.004182 at  $20^{\circ}$ . It contains in 1000 parts:  $\text{Na}_2\text{CO}_3$ , 0.200786;  $\text{Li}_2\text{CO}_3$ , 0.010135;  $(\text{NH}_4)_2\text{CO}_3$ , 0.003693;  $\text{K}_2\text{SO}_4$ , 0.028505;  $\text{KCl}$ , 0.015267;  $\text{NaCl}$ , 1.889081;  $\text{NaBr}$ , 0.000854;  $\text{NaI}$ , 0.000017;  $\text{Na}_2\text{HPO}_4$ , 0.000302;  $\text{CaCO}_3$ , 0.779638;  $\text{MgCO}_3$ , 0.359795;  $\text{FeCO}_3$ , 0.008784;  $\text{MnCO}_3$ , 0.003115;  $\text{SiO}_2$ ,  $0.020180 = 3.320152$ ;  $\text{CO}_2$  in bicarbonates, 0.627025; free  $\text{CO}_2$ , 2.58583. Also traces of barium, strontium, alumina, and boric acid. It is an acid water containing much sodium chloride and carbonates of calcium, &c. L. J. S.

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## Physiological Chemistry.

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**Relation of the Blood to the Automaticity and Sequence of the Heart-beat.** By WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1898, 2, 47—81).—A strip of vena cava from the terrapin's heart may be kept in rhythmic action for 2 days or more, when immersed in a bath containing only sodium chloride, potassium chloride, and calcium chloride; this fact renders improbable Kronecker's theory, that the cardiac tissue beats only so long as serum-albumin is supplied to it. The energy is evidently derived from material within the cardiac tissue, and if supplied with an adequate stimulus, the beat will continue until this is consumed. The normal stimulus is dependent on calcium compounds, but for rhythm, potassium salts are also necessary. The proportion of the three salts necessary is that which occurs in the blood, and the sodium chloride must be isotonic with the blood, and is essential only to preserve the normal osmotic relations between the tissues and the surrounding liquid.

Such a liquid will not keep the ventricle of frog or terrapin in action, although it will that of the cardiac tissue at the venous end of the heart. The normal heart's rhythm is, therefore, started at the venous end, because that part of the heart is alone susceptible to the salts of the blood.

W. D. H.

**Relation of the Inorganic Salts of the Blood to the Automatic Activity of Ventricular Muscle.** By CHARLES WILSON GREENE (*Amer. J. Physiol.*, 1898, 2, 82—126).—Normal serum will not keep a strip of the apex of the terrapin's heart in contraction, although it remains alive for several days. Regular contractions may, however, be produced by increasing the amount of calcium chloride in the serum. The same is true for a solution of the blood salts (like Ringer's fluid) similar to those used by Howell (see preceding abstract). Sodium chloride will sustain contractions only for a short time, and these present the appearance of fatigue owing to the removal

of the inorganic salt necessary for contraction. Calcium salts in isotonic solutions of sodium chloride stimulate the strip to increased rhythm and final contracture. Potassium chloride in a similar solution produces relaxation.

Cane-sugar and urea in isotonic solutions do not produce rhythmic contractions in the isolated strip; dextrose increases muscular tone and may produce an imperfect series of contractions. W. D. H.

**Functions of the Thyroid Gland.** By F. BLUM (*Zeit. physiol. Chem.*, 1898, 26, 160—174).—The paper is largely critical. The author believes the thyroid is an excretory organ removing poisonous substances from the blood, and that the iodine formed there originates in that way. He regards the iodine as in organic union with proteid material, and iodothyryl as an artificial product. W. D. H.

**Active Physiological Substance of the Suprarenal Capsules.** By OTTO VON FÜRTH (*Zeit. physiol. Chem.*, 1898, 26, 15—47).—Various methods are described in which an attempt was made to isolate the active substance in extracts of the suprarenal capsules. Although the author still continues to speak of the material as catechol-like, he admits that Moore is right when he places the substances among the derivatives of pyridine. He suggests with reserve that it is a hydrogenised dihydroxypyridine. W. D. H.

**Æolosomin.** By ARTHUR BOWER GRIFFITHS (*Compt. rend.*, 1898, 127, 448—449).—The cellules of *Æolosoma tenebrarum* contain a green pigment which has a respiratory function. It dissolves in acids, forming a green solution which is coloured purple by alkalis, but changed back again to green by excess of acid. It also dissolves in turpentine. The solutions of the pigment show no definite absorption bands.

Æolosomin exists in two forms, æolosomin and oxyæolosomin; the empirical composition of the former is  $C_{420}H_{630}N_{103}FeS_2O_{152}$ . C. H. B.

**Human Milk.** By VANDERPOEL ADRIANCE and JOHN S. ADRIANCE.—This pamphlet records analyses of 200 specimens of human milk obtained by the breast pump. These are arranged according to the time after parturition. The fat is variable, and shows no constant change. The lactose on the second day of lactation is low, but then rises rapidly; this increase continues more slowly until the end of lactation; the proteids and salts pursue a reverse course. In the later months of lactation, the total solids decrease steadily. The colostrum period has low carbohydrate with a tendency to increase rapidly, and high proteids and salts with a tendency to decrease rapidly.

In cases of abnormal milk, excessive fats or proteids, especially during the colostrum period, cause gastro-intestinal symptoms in the child. The excess in the milk may be reduced by diminishing the proteid food, and increasing the exercise of the mother. Deterioration in the milk is marked by reduction in proteids and total solids, or in

the proteids alone. Such deterioration is normal in the later months, and indicates that additions to the infant's diet are necessary.

W. D. H.

**Supposed Existence of Iodine in Organic Combination in the Urine after the Administration of Potassium Iodide.** By DIOSCORIDE VITALI (*L'Orosi*, 1898, 21, 145—153).—The urine excreted by subjects to whom pure potassium iodide had been administered was treated with baryta water to remove phosphates and urates, the chlorides and iodides precipitated by silver nitrate, the excess of the latter removed by means of sodium chloride, and the filtered liquid mixed with caustic potash and potassium nitrate and evaporated to dryness. No iodine could be detected in the fused residue until after reduction with sulphurous acid, the whole of the "organic iodine" having been converted into iodate by the large excess of nitrate. Chlorides, under the same conditions, are partially converted into chlorates, and this fact may account for the discrepancies between the statements made by different observers as to the existence of "organic chlorine" in urine. Experiments were made to ascertain whether the "organic iodine" was present as iodoic acid, by extracting the concentrated and acidified urine with ether. By this process, organic compounds containing iodine were certainly obtained, but they were formed during the extraction, since similar results were obtained with normal urine to which potassium iodide had been added. The author concludes that, although organic iodine compounds may, perhaps, be formed in certain organs and tissues of the body, yet the iodine contained therein passes into the urine in the form of alkali iodides which may subsequently, after excretion, undergo decomposition with the formation of organic compounds of iodine.

N. L.

**Organic Phosphorus in Urine.** By HORST OERTEL (*Zeit. physiol. Chem.*, 1898, 26, 123—130).—Several previous observers have realised that all the phosphorus in the urine is not combined as phosphoric acid, but that there are organic compounds like glycerophosphates present.

The total phosphorus may be estimated as phosphate after fusing the dry residue of the urine with potassium hydroxide and nitrate. The organic phosphorus may be similarly estimated after precipitating the inorganic phosphates with calcium chloride and ammonia.

If the total phosphates in the day's urine amount to 2 grams, 0.05 gram comes from the organic phosphorus compounds; this varies, however, with nitrogenous metabolism; muscular exercise has no effect on it.

W. D. H.

**Uric Acid and the Acidity of Urine.** By W. J. SMITH JEROME (*J. Physiol.*, 1898, 23, 315—324).—The urine in healthy persons may be made to deposit uric acid by the ingestion of a sufficient quantity of food rich in nuclein. Some urines after an ordinary diet have an abnormal tendency to the precipitation of uric acid; this tendency is not always due either to a high degree of acidity, or to a high percentage of uric acid in the urine, or to the co-existence of these two conditions, however much such conditions may favour the precipitation.

W. D. H.

**Uric Acid and Diet.** By F. GOWLAND HOPKINS and W. B. HOPE (*J. Physiol.*, 1898, 23, 271—295).—Experiments on seven persons confirm Marés' statement that, during the period of increased nitrogen excretion that follows a meal, the rise in uric acid has a shorter duration than that of urea, and occurs in the earlier hours of this period. This is difficult to reconcile with the view that the acid originates from the nuclein of the diet, on which the earlier stages of digestion have only a minimal effect.

The chief evidence in favour of the view that nucleins play a rôle as precursors of uric acid is based upon the results of thymus feeding. The present experiments show that extracts may be prepared from this gland which contain only traces of nuclein and nucleic acid, but when injected they produce a large excretion of uric acid. It therefore appears that some more soluble constituent of the diet acts either as a direct precursor or as a factor in a synthetic process.

W. D. H.

**Dichlorothymolglycuronic Acid.** By K. KATSUYAMA and S. HATA (*Ber.*, 1898, 31, 2583—2585).—Rabbits were fed with thymol and their urine treated with hydrochloric acid and sodium hypochlorite (Blum, *Zeit. physiol. Chem.*, 1895, 16, 514). In this way, a product was eventually obtained which was identical with Blum's dichlorothymolglycuronic acid, except that it melted at 118° instead of 125—126°. Its *barium* salt,  $(C_{16}H_{21}Cl_2O_8)_2Ba$ , was prepared and analysed; when boiled with dilute sulphuric acid, the acid gave glycuronic acid and a substance containing chlorine.

Rabbits, then, like men and unlike dogs, excrete thymolglycuronic acid; they are able to bring about a combination of thymol with the glycuronic acid of their bodies.

C. F. B.

**Excretion of Kynurenic Acid.** By LAFAYETTE B. MENDEL and HOLMES C. JACKSON (*Amer. J. Physiol.*, 1898, 2, 1—28).—The experiments made on dogs, which are recorded, gave the following results. Kynurenic acid is a direct product of proteid katabolism, and as Baumann indicated, it does not originate as the result of putrefaction in the intestines. Its amount in the uriae rises with proteid katabolism, whether this is produced by starvation, excess of proteid food, or the drugs borax and phloridzin; gelatin and carbohydrates do not act in this way. In conditions of nitrogenous equilibrium, or under the influence of proteid-sparing foods, the excretion of the acid is diminished or absent.

Uric acid and kynurenic acid may occur together in dog's urine, as Solomin found. Kynurenic acid was not found in the urine of cats and rabbits.

The observations suggest the presence of a quinoline-like radicle in the proteid molecule; the existence of a large carbohydrate group is also confirmed.

W. D. H.

**Modification of Rigor Mortis by Fatigue.** By CAROLINE W. LATIMER (*Amer. J. Physiol.*, 1898, 2, 29—46).—After prolonged fatigue from electrical stimulation, the muscles of cold-blooded animals

enter into rigor much earlier, and shorten much less than when not fatigued.

This is not due to increase of lactic acid, of carbonic anhydride, or other fatigue products, or to the abstraction of calcium salts, but to the exhaustion of the glycogen normally present in muscle, for the circulation through the exhausted muscle of a liquid containing dextrose in the proportion normally present in the blood effects a more or less complete restoration of the normal rigor.

W. H. D.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Action of Oxygen on Beer Yeast.** By JEAN EFFRONT (*Compt. rend.*, 1898, 127, 326—327).—When pressed beer yeast is exposed to the air, it absorbs oxygen with considerable development of heat, and with 2 kilos. of yeast in layers 37 cm. high, the temperature rises from 20° to 56°. This fact may be utilised for the detection of oxygen in a mixture of gases; the gas to be examined is passed very slowly through a mixture of yeast and pumice in which a thermometer is embedded, and the presence of oxygen is indicated by a rise of temperature.

The phenomenon is due to the presence in the cellules of an oxidising enzyme, which will be described subsequently. C. H. B.

**Poisonous Effects of Cupric Salts on Higher Plants.** By HENRI COUPIN (*Compt. rend.*, 1898, 127, 400—401).—Experiments on young wheat plants lead to the following *toxic equivalents*, which represent the minimum quantity of the salt that must be dissolved in 100 parts of water in order to kill the plants: cupric bromide, 0·004875; chloride, 0·005000; sulphate, 0·005555; acetate, 0·005714; nitrate, 0·006102. It seems clear that the toxic effect is due to the copper ion, and that the electronegative radicle is practically without influence.

It follows from these results that the use of *solutions* of cupric salts as germicides is attended with considerable risk. C. H. B.

**Composition and Feeding Value of Millet.** By BALLAND (*Compt. rend.*, 1898, 127, 239—240).—The term *millet* is applied commercially to grains derived from several different plants. Common or paniculated millet forms brilliant, ovoid, white, yellow, red, or black grains, which weigh from 4·60 to 5·90 grams per 1000. It has been grown from pre-historic times in middle Europe, Egypt, and Asia. Awmed millet, or *panic* millet, which is sometimes erroneously described as *Panicum italicum*, forms small, round, straw-coloured grains, 1000 of which weigh about 2·65 grams. Like common millet, it has been grown in temperate climates and used as human food since pre-historic times. Long millet forms elongated, greyish-yellow grains, with a smooth, highly lustrous envelope; they are much larger than the grains of common millet, and 1000 weigh 7·0 to 8·2 grams.

Like maize, millet is rich in fat and nitrogen, and is physiologically a more complete food than wheat; whilst millet contains less cellulose than African millets, and the latter contain more nitrogen. A number of millets from Africa, France, Italy, and Turkey were found to show the following extremes of composition. Water, 10.10 to 13.00; nitrogenous compounds, 8.98 to 15.04; fats, 2.20 to 7.30; sugar and starches, 57.06 to 66.33; cellulose, 3.00 to 10.23; ash, 1.40 to 6.00 per cent.; acidity, 0.055 to 0.098 per cent. C. H. B.

**Phosphoric Acid dissolved by the Water in Soils.** By TH. SCHLOESING, Jun. (*Compt. rend.*, 1898, 127, 236—239 and 327—329).—The quantity of phosphoric acid dissolved in the water impregnating soils is usually about 1 milligram per litre, but sometimes is as much as 2 or 3 milligrams. Estimation of the phosphoric acid in the water displaced from various soils by the method of Schloesing, sen., shows that the proportion of phosphoric acid in solution depends on the nature of the soil, but is independent of the proportion of water in the soil. The quantity of phosphoric acid that remains in solution is the result of equilibrium between complex reactions, some of which tend to withdraw the acid from the solution, and, in most cases, the quantity dissolved is very small compared with the total quantity in the soil. It follows that, as fast as the dissolved acid is removed by vegetation, a corresponding quantity passes into solution from the soil, and hence, although the quantity dissolved at any particular instant is small, the total quantity brought to the roots of a plant during its life-time may be considerable.

The method of displacement involves the use of large quantities of soil and has other inconveniences, and in most cases the quantity of dissolved phosphoric acid can be estimated more quickly and easily. Agitation with water for 10 hours is quite sufficient to ensure the dissolution of the maximum proportion of phosphoric acid, and it is not advisable to agitate for a longer time, because secondary reactions may cause the reprecipitation of part of the acid. Further, although the proportion of acid dissolved increases with the ratio of soil to water, the increase is practically negligible if the proportion of dry soil is not less than 300 grams to 1300 c.c. of water. It is advisable, therefore, to take soil and water in these proportions. Carbonic anhydride has no influence on the result, provided that it is not in excess with respect to the calcium carbonate present. C. H. B.

**Constitution of Natural Humoid Substances.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1898, 127, 414—417).—The author has subjected various soils to the action of dilute acids and alkalis, with a view to throw light on the constitution of the nitrogenous organic matter that they contain. The soils were a cultivated soil, moorland soil, leaf-mould, and peat, and they were heated at 100° for 15 hours with potassium hydroxide or hydrochloric acid in quantity equal to twenty times the weight of the total nitrogen present, the acid or alkali being diluted with thirty times its weight of water. The nitrogenous matter insoluble in the alkali was afterwards treated with the acid, and *vice versa*. In the case of the alkali, the author estimated the nitrogen in four distinct forms, (1) evolved as



ammonia, (2) insoluble in alkali, (3) soluble in alkali and not precipitated by acids, (4) soluble in alkali and reprecipitated by acids. After treatment with the acid, he estimated the nitrogen (1) insoluble in acid, (2) existing as ammonia, (3) existing as amides. The results are given in tabular form.

The peat and the cultivated soil, when treated with alkali, yield a larger proportion of their nitrogen in the form of ammonia than the moorland soil or vegetable mould. The percentage of total nitrogen rendered soluble by the alkali is: peat, 79.19; cultivated soil, 76.92; moorland soil, 74.84; leaf-mould, 72.95, but the soluble nitrogen not precipitated by acid is higher in the cultivated soil and leaf-mould than in the other two. On the other hand, the percentage of total nitrogen rendered soluble by hydrochloric acid is: cultivated soil, 61.52; moorland soil, 61.70; peat, 53.91; leaf-mould, 39.34; and the proportion of ammoniacal nitrogen obtained is lower than when treated with alkali.

The different order in which the soils arrange themselves when treated by different reagents indicates that their nitrogenous matters differ in constitution.

C. H. B.

**Action of Calcium Oxide and Carbonate on certain Humoid Substances.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1898, 127, 446—448).—The four soils used in experiments with dilute acid and alkali (preceding abstract) were heated at 100° for 15 hours with calcium oxide, calcium carbonate, or water only, and the nitrogen volatilised and the nitrogen rendered soluble were determined. The soils were also allowed to remain in contact with calcium oxide at the ordinary temperature for 82 days, with occasional agitation. The results are stated in the form of a table.

The quantity of ammonia liberated by the action of calcium oxide at 100° is considerable, but is lower than that liberated by potassium hydroxide. Calcium carbonate, and even water alone, cause the liberation of ammonia from all the soils, and in the case of the cultivated soil and peat the quantity is not negligible. The cultivated soil is more completely attacked than the other three by calcium oxide at 100°, and this is true also of calcium carbonate at 100°.

The quantity of nitrogen converted into ammoniacal nitrogen by the action of calcium oxide at the ordinary temperature amounts to from 5 to 6 per cent. of the total nitrogen in all four cases, and this indicates that the nitrogen of the amides in the soil is partially converted into ammoniacal nitrogen under the conditions specified, whatever may be the nature of the original nitrogenous matter.

C. H. B.

**Nitrogenous Substances accompanying Humic Acid in the Soil.** By FAUSTO SESTINI (*L'Orosi*, 1898, 21, 1—6).—The humic acid extracted from soil always contains notable quantities of nitrogenous substances, other than ammonia, which are more or less completely removed when the crude substance is purified by repeated dissolution in alkalis and reprecipitation with hydrochloric acid. These impurities are readily decomposed by concentrated alkalis, but on boiling crude humic acid with 2 per cent. sodium hydroxide solution

for  $13\frac{1}{2}$  hours little more than half the nitrogen is expelled as ammonia. Dilute hydrochloric acid effects no sensible decomposition, and only a relatively small amount of ammonia is formed by boiling with 10 per cent. hydrochloric acid for 24 hours. It is concluded from these results that the nitrogen accompanying humic acid does not exist, to any large extent, in the form of amides. Experiments on the action of nitrous acid indicate the presence of appreciable amounts of amido-acids, but this question is reserved for further study. Previous observations by the author on the production of furfuraldehyde by the action of hydrochloric acid on humic acid have led him to suppose that the nitrogenous substances accompanying the latter might contain a pentosan residue. It is now found that furfuraldehyde is yielded, not only by crude humic acid, but also by the purified product, and, although to a less extent, by the humous substances formed by the action of mineral acids on pure sugar.

N. L.

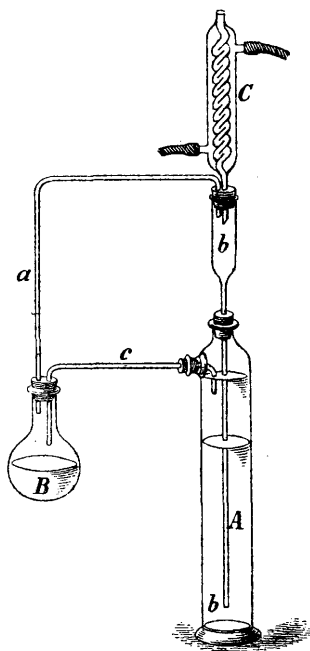
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## Analytical Chemistry.

**Extraction of Liquids.** By OTTO FOERSTER (*Chem. Zeit.*, 1898, 22, 421—422).—The apparatus is intended for the extraction of unsaponifiable matter from soapy liquids.

The soap solution, which should be nearly free from alcohol and measure about 600 c.c., is introduced into the detached cylinder *A*, 300 c.c. of ether is added, the stoppers are put in, and the whole is thoroughly shaken. When the two layers have separated, the stoppers are removed and well rinsed with ether; the top part of the cylinder is also rinsed. The other parts of the apparatus are then connected. *B* is a distilling flask of 200—300 c.c. capacity, partially filled with ether, and furnished with a cork having two perforations, the flask being heated by hot water. The ether vapour passes through the tube *a* into *b*, and when condensed in *C* runs through *b* to nearly the bottom of *A*, and then ascending, gradually increases the volume of ether until it overflows into the flask *B* by means of the syphon tube *c*.

The extraction is complete within 4 hours. As soap is not quite insoluble in ether, this must be afterwards shaken four times in succession with a little



water to remove the soap. In order to ascertain the accuracy of the process, 1 gram of cholesterol was added to a solution of soap previously extracted with ether and 0.9997 gram was recovered.

L. DE K.

**A New Form of Crucible. The Tube Crucible.** By ERNST MURMANN (*Monatsh.*, 1898, 19, 403).—The bottom (*b*) of this crucible is perforated and furnished with a straight (*c*) or bent (*c*) tube, which serves the twofold purpose of conducting away a liquid from a precipitate or allowing the passage of a gas over the precipitate while the crucible is heated. The retention of the precipitate is provided for by placing a layer of asbestos between the bottom of the crucible and a sieve-plate which is of somewhat smaller size.

The crucible may be used in the estimation of many metals, and is of especial advantage in the case of the estimation of zinc or manganese as sulphide (see this vol., ii, 126).

A. L.

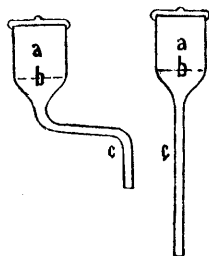
**Quantitative Separation of Halogens.** By RALPH S. SWINTON (*Pharm. J.*, 1898, 59, 562—564).—The amount of iodine in any mixture of soluble haloid salts is determined by successively adding to an aqueous solution, containing a known quantity of the mixture, strong sulphuric acid, phenol, and bromine water. The mixture is thoroughly agitated and then extracted with chloroform, which removes the liberated iodine. This treatment is repeated in order to decompose all the iodide present; in each case, the excess of bromine combines with the phenol to form tribromophenol. The chloroform extract is mixed with water, and titrated with sodium thiosulphate in the usual manner.

In the absence of iodides, the amount of bromine present in a mixture is obtained by agitating its solution in cold sulphuric acid with potassium permanganate and chloroform. The solution of bromine in chloroform is added to alcoholic potassium iodide; the amount of iodine set free and estimated by thiosulphate is a measure of the bromine originally present in the solution.

Three determinations are required in order to ascertain the amount of chlorine, bromine, and iodine in a mixture of the haloid salts. The iodine is determined in one portion by the method described above. From another portion, the iodine is liberated by means of the calculated amount of  $N/2$  potassium permanganate and extracted by chloroform; the bromine is then liberated by the addition of excess of permanganate, and its solution in chloroform mixed with alcoholic potassium iodide, to which the chloroform extract of iodine is subsequently added, and the whole diluted with water and titrated with thiosulphate. Lastly, a portion of the original mixture is titrated with standard silver nitrate solution, using potassium chromate as indicator.

These three determinations furnish sufficient data for the estimation of the halogens in any mixture of their salts.

G. T. M.



**Quantitative Electrolytic Separation of Chlorine, Bromine, and Iodine.** By H. SPECKETER (*Zeit. Elektrochem.*, 1898, 4, 539).—When a normal solution of hydriodic acid is electrolysed with a silver anode and a platinum cathode, silver iodide is formed, and hydrogen eliminated with an E.M.F. of  $-0.06$  volt, hydrobromic acid requires  $+0.15$  volt, and hydrochloric acid  $0.3$  volt. More dilute solutions require greater E.M.F.'s. Oxygen must be absent otherwise the combination develops an E.M.F. of more than  $1$  volt, and all the halogens separate out. The silver employed must be pure. In practice, a solution in normal sulphuric acid is used and an anode of pure silver gauze, the electrolysis being conducted in a current of hydrogen. With  $0.13$  volt, the iodine is almost completely separated as silver iodide which adheres firmly to the anode, and may be washed and weighed together with it;  $0.35$  volt separates bromine in the same way, the chlorine remaining being titrated as usual. The greater part of the results given are accurate to within  $0.5$  per cent.

T. E.

**Application of Phloroglucin-vanillin for the Detection of Sulphur and Nitrogen in Organic Compounds.** By P. N. RAIKOW (*Chem. Zeit.*, 1898, 22, 377—379).—The author (this vol., ii, 52) finds that an ethereal solution of phloroglucinol-vanillin not only readily detects halogens in organic compounds, but that it is also an excellent reagent for the detection of organic sulphur and some forms of organic nitrogen.

To detect sulphur in commercial oils, an open glass tube is bent at right angles near one end, a few drops of the oil are introduced at the bend, a wick of long-fibre asbestos is then introduced, and the oil is burnt, oils which give off much soot being diluted with alcohol or ether; the products of combustion are allowed to act on a porcelain crucible lid moistened with the reagent. In the presence of sulphur, sulphuric acid is formed which gives a characteristic red spot. A yellow spot is obtained by the combustion of amines, hydrazines, and similar nitrogenous compounds, and if halogens or sulphur should also be present, both kinds of spots are visible. This is the case with such substances as wool, hair, goose-feathers, casein, and artificial products such as thiocarbamide, sulphanilic acid, magenta, methyl-violet, &c.

L. DE K.

**Colour Reaction of Anhydrosulphuric Acid.** By ETIENNE BARRAL (*Bull. Soc. Chim.*, 1897, [iii], 17, 744—745).—Hexachlorobenzene paradichloride slowly dissolves in sulphuric acid containing anhydrosulphuric acid, with the production of a fine, red-violet coloration. The reaction is not given by dry sulphuric anhydride, but, on exposure to a moist atmosphere, the coloration quickly appears, and is finally destroyed when sufficient water or dilute sulphuric acid is added to convert the whole of the sulphuric anhydride present into ordinary sulphuric acid. The colour changes are sufficiently sharp to admit of the volumetric estimation of anhydrosulphuric acid by titration with dilute sulphuric acid of known strength. In the case, however, of commercial Nordhausen sulphuric acid, which is usually more

or less coloured, the end-point is somewhat obscure, and the results are wanting in accuracy.

N. L.

**Detection of Sulphides, Sulphites, Sulphates, and Thiosulphates in the presence of each other.** By PHILIP E. BROWNING and ERNEST HOWE (*Amer. J. Sci.*, 1898, [iv], 6, 317—322; and *Zeit. anorg. Chem.*, 18, 371—377).—This is a modification of the scheme recommended by Greig Smith (*Abstr.*, 1896, ii, 71). To about 0.1 gram of the mixture, dissolved in 10 c.c. of water, ammonia is added until distinctly alkaline, the sulphide is then precipitated with zinc acetate, and the precipitate is further examined. The filtrate is slightly acidified with acetic acid, any sulphate is precipitated by barium chloride, the solution filtered, and the filtrate mixed with a very slight excess of iodine; stannous chloride is added until the colour of the iodine disappears, and then a few drops of hydrochloric acid; a precipitate proves the presence of a sulphite. The filtrate from this is mixed with excess of bromine water, and stannous chloride is added until the liquid is decolorised; a precipitate indicates the presence of a thiosulphate.

L. DE K.

**Modifications of Kjeldahl's Process.** By ALBERT ATTERBERG (*Chem. Zeit.*, 1898, 22, 505—506).—The author heats 0.5 gram of the nitrogenous compound with 20 c.c. of strong sulphuric acid and a drop of mercury, and, when frothing has ceased, 15 to 18 grams of potassium sulphate is added; the liquid is generally colourless after 30 minutes boiling, but it is advisable to boil for another 15 minutes. Treated in this manner, even quinine yields the whole of its nitrogen in the form of ammonia.

Attempts to replace the mercury by other metals or oxides were not quite successful. Phosphoric anhydride has no advantage over potassium sulphate. Molybdic acid acts energetically, but, on account of the blue colour of the solution, it is difficult to observe the end reaction.

L. DE K.

**Estimation of Arsenic in Antimony and in Metals.** By O. DUCRU (*Compt. rend.*, 1898, 127, 227—229).—About 5 grams of the coarsely powdered substance is distilled with 100 c.c. of ferric chloride solution and 200 c.c. of concentrated hydrochloric acid until 100 c.c. has passed over. A further quantity of 100 c.c. of hydrochloric acid is then added, and a second 100 c.c. distilled off, after which the same treatment is repeated, so that the total volume of the distillate is 300 c.c. The end of the condenser tube should dip into the distillate, and about 50 c.c. of water should be placed in the receiver at the beginning of the operation.

The distillate contains a little antimony, and must therefore be redistilled until about 300 c.c. has passed over. If 50 to 100 c.c. of concentrated sulphuric acid is added before redistilling, it is usually sufficient to collect 150 c.c. The arsenic in the final distillate is precipitated with hydrogen sulphide in the usual way.

The ferric chloride solution is prepared by allowing 2000 c.c. of hydrochloric acid and 2000 c.c. of water to act on 800 grams of French nails, and, after all action has ceased, the liquid is saturated

with hydrogen sulphide and filtered. The excess of hydrogen sulphide is expelled by boiling, and a current of chlorine is passed into the liquid until all the iron is oxidised. The excess of chlorine is afterwards expelled by means of a current of air, and the liquid is diluted to 5000 c.c. by adding concentrated hydrochloric acid. The solution should be examined for arsenic by distilling some of it, after adding 15 grams of ferrous sulphate free from arsenic.

The method is applicable to many metals, such as iron, steel, lead, tin, zinc, and alloys, as well as to antimony. C. H. B.

**Methods for Estimating Potassium, and the Best Precipitants of Platinum.** By ALBERT ATTERBERG (*Chem. Zeit.*, 1898, 22, 522—523; 538—539).—It is admitted that, instead of weighing the potassium platinochloride, it is better to dissolve the compound in boiling water and to reduce the platinum by suitable means; the metal is then collected, weighed, and calculated to potassium. For this purpose, the author prefers using magnesium ribbon, the excess of which may be readily removed by hydrochloric acid. If the amount of platinum is very small, thioacetic acid is recommended.

When potassium is separated from sodium, the latter is left in the alcoholic filtrate containing also the excess of platinum chloride. If it be desired to directly estimate the sodium, the author recommends removing the platinum by means of metallic mercury at the boiling temperature. The liquid then contains some mercuric chloride, which is readily separated from the sodium chloride by heating the dry residue.

To avoid the tedious separation of iron or aluminium before treating the sample with platinum chloride, the author recommends adding some citric acid; the acid citrates of iron and aluminium are readily removed by washing with alcohol. L. DE K.

**Electrolytic Deposition of Silver from Solutions in Nitric Acid.**—By FRIEDRICH W. KÜSTER and H. VON. STEINWEHR (*Zeit. Elektrochem.*, 1898, 4, 451).—The authors have experienced great difficulty in obtaining a smooth deposit of silver from solutions of the nitrate by the processes hitherto prescribed; a spongy deposit was almost invariably formed after some time. In all these cases, they attempted to work with the prescribed constant current, the result being that, as the amount of silver in the solution diminished, the E.M.F. required increased. A very large number of experiments were then carried out in which the E.M.F. was kept constant and the current allowed to vary. The formation of silver peroxide is easily prevented by the addition of a little alcohol. The result finally arrived at is that a perfect deposit of silver may be obtained with certainty by adding 1 to 2 c.c. of nitric acid of sp. gr. = 1.4 and 5 c.c. of alcohol to the solution, and electrolysing at 55° to 60° with a constant E.M.F. of 1.35 to 1.38 volts. With 1.4 volts or more, the deposit becomes spongy, even when the other precautions are taken. As much as 2 grams of silver may be deposited. The constant E.M.F. was obtained by short-circuiting a Gölcher thermo-battery by a resistance small enough to reduce its E.M.F. to the desired value. The terminals of the electrolytic cell are then connected to those of the battery. The usual plan of putting a resistance in series with the electrolytic

cell so as to reduce the E.M.F. between the electrodes to the desired value is unsuitable because, as the electrolysis progresses, the resistance of the cell increases, and with it the E.M.F. Test analyses of a silver coin carried out by the method described, gave results varying from 89.75 to 89.83 per cent. of silver, the mean, 89.79, being practically identical with the mean of two very careful gravimetric determinations (89.789). T. E.

**Estimation of Zinc and Manganese as Sulphides.** By ERNST MURMANN (*Monatsh.*, 1898, 19, 404—405).—The estimation of zinc and manganese as sulphides is not in general use, owing to the difficulty of obtaining a clear filtrate and the lengthy washing which is necessary. The author avoids these difficulties by precipitating the sulphides in presence of mercuric chloride, when the mercuric sulphide which is formed largely increases the bulk and conspicuousness of the precipitate and renders it more easy to filter and wash. The precipitate is collected in a "tube-crucible" (see this vol., ii, p. 122) and heated in a stream of hydrogen as usual, when the mercuric sulphide is completely volatilised.

The same method may be employed in the case of stannic hydrate, and is probably applicable to other precipitates. A. L.

NOTE.—Lowe has shown that there is no difficulty in the filtration of zinc sulphide if the precipitation is effected with the proper precautions (*Abstr.*, 1893, ii, 302). EDITORS.

**Electrolytic Separation of Cadmium and Iron.** By WILLEM STORTENBEKER (*Zeit. Elektrochem.*, 1898, 4, 409).—The mixture of cadmium and iron salts is dissolved in 100 c.c. of water, and, if more than a trace of ferric salt is present, reduced by adding about five times the requisite quantity of sodium sulphite to the slightly acid solution and warming. Two or three grams of pure potassium cyanide are now added, and the solution warmed until it takes the yellow colour of potassium ferrocyanide; it is then diluted to 200—250 c.c., and electrolysed overnight at the ordinary temperature with 0.05 to 0.1 ampère per sq. decm. The results are excellent. T. E.

**Electrolytic Separation of Copper from Silver, Mercury, and Arsenic.** By N. REVAY (*Zeit. Elektrochem.*, 1898, 4, 313 and 329).—*Copper and Silver.*—In order to decompose a solution of silver nitrate, an E.M.F. of about 0.9 volt is needed, whilst for copper nitrate the value is approximately 1.4 volts; when a solution containing silver and copper nitrates is electrolysed at about 70° with from 1.3 to 1.4 volts, the silver is deposited, the copper remaining in solution. The deposit obtained is not quite smooth, but adheres sufficiently well to the platinum dish to allow of its being washed; at lower temperatures, this is not the case. The solution must be strongly acidified with nitric acid in order to prevent the formation of silver peroxide. In presence of potassium cyanide, the cathodic polarisation, both of silver and copper, is much higher than in acid solution, owing to the smaller number of ions present. It also increases as the concentration of the metal diminishes, so that, from



solutions containing much copper and little silver, the former may be more readily deposited than the latter. At 45—60°, however, with 1.65—1.8 volts, the author obtains very satisfactory results, the deposit of silver being smooth and adherent.

*Copper and Mercury.*—The E.M.F. required to deposit mercury is almost the same as that required for silver under similar circumstances. From acid solutions of copper sulphate and mercuric chloride, deposits of mercury, apparently contaminated with mercurous salts, were thrown down, and no results of value were obtained with solutions of mercurous nitrate in presence of nitric acid. In solutions containing potassium cyanide, mercury behaves in much the same way as silver. When the concentration of the mercury falls below about 1/384 normal, potassium is more easily separated at the cathode than mercury, and hydrogen is therefore evolved. When the concentration of the copper is not too great, however, a satisfactory separation is possible, using 1.8—1.95 volts at the ordinary temperature. In the experiments quoted, 0.5 to 0.6 gram of crystallised copper sulphate was mixed with 3 grams of potassium cyanide, and from 0.25 to 1.0 gram of mercuric chloride; the mercury found was 0.1 to 0.2 per cent. too low.

*Copper and Arsenic.*—From solutions of copper sulphate and potassium arsenate acidified with sulphuric acid, the copper is readily deposited in a pure state by 1.6 to 1.8 volts in 16 to 24 hours. The separation is also a good one in ammoniacal solution, 9 to 20 hours being required with 1.65 to 1.8 volts.

T. E.

**Separation of Nickel from Cobalt by Hydrogen Chloride.** By FRANK S. HAVENS (*Zeit. anorg. Chem.*, 1898, 18, 378—381).—The method described by E. Piñerúa (*Abstr.*, 1897, ii, 387) which is based on the insolubility of nickel chloride in ether saturated with hydrogen chloride is not accurate. Piñerúa precipitates the nickel chloride in a mixture of equal parts of concentrated hydrochloric acid and dry ether saturated with hydrogen chloride, but the author finds that 14 c.c. of such a solution contains 0.002 gram of metallic nickel. An accurate separation of nickel and cobalt chlorides can be effected by a modification of this method, provided that only a few centigrams of cobalt chloride are present, but when more cobalt chloride is present, the nickel chloride always carries down with it an appreciable quantity of cobalt which cannot be washed out of the precipitate with ether saturated with hydrogen chloride. The separation is carried out as follows. The solution of the chlorides is evaporated to dryness, dissolved in the smallest possible quantity of water (about 1 c.c.) 10—15 c.c. of dry ether added, and the cooled solution saturated with hydrogen chloride. The precipitate formed is washed with ether saturated with hydrogen chloride, and the nickel in the precipitate and the cobalt in the filtrate are then estimated by electrolysis. It is probable that, in the presence of larger quantities of cobalt, a complete separation could be obtained by repeated precipitation of the nickel chloride.

E. C. R.

**Electrolytic Separation of Cobalt and Nickel.** By ALFRED COEHN (*Zeit. Elektrochem.*, 1898, 4, 501).—The author shows that electro-stenolysis occurs in the following cases: (a) the negative

radicle separated at the anode does not act on the metal deposited at the cathode ; (b) insoluble compounds such as peroxides are formed at the anode ; (c) the radicle separated at the anode combines with the solution, as, for example, in a solution of cuprous chloride. He has observed that the cobalt salts exhibit stenolysis, whilst those of nickel do not ; the difference is due to the deposition of cobaltic oxide at the anode, nickel salts giving no such deposit ; this behaviour may be utilised for the separation of the metals. The electrolysis is carried out in neutral solution, copper sulphate being added in order to prevent the deposition of part of the cobalt at the cathode.

T. E.

**Estimation of Manganese as Pyrophosphate.** By FRANK A. GOOCH and MARtha AUSTIN (*Amer. J. Sci.*, 1898, 6, 233—243, and *Zeit. anorg. Chem.*, 18, 339—351).—The accuracy of this process depends a good deal on the amount of ammonium salts and free ammonia present, and the authors, after a lengthy investigation, now propose the following process. The liquid, which should be slightly acid and contain an amount of manganese not exceeding that which would produce 0.4 gram of pyrophosphate, is diluted to 200 c.c., and 20 grams of ammonium chloride and 10 c.c. of a cold saturated solution of sodium ammonium phosphate are added. After adding dilute ammonia in very slight excess, the mixture is heated until the precipitate which is formed becomes silky and crystalline ; after being allowed to cool for half an hour, the precipitate is collected on a Gooch's crucible, washed with slightly ammoniacal water, dried, ignited, and weighed as pyrophosphate.

L. DE K.

**Estimation of Oxide of Iron and Alumina in Phosphates.** By N. BLATTNER and J. BRASSEUR (*Bull. Soc. Chim.*, 1897, [iii], 17, 760—761).—A critical examination of the methods commonly employed for the estimation of oxide of iron and alumina in phosphates has led the authors to the following conclusions. The acetic method, as modified by Maret and Delattre, should be rejected as giving low results, since a portion of the alumina always remains in solution. Glaser's method is rapid, easy of execution, and gives sufficiently accurate results in the case of phosphates free from manganese. The method involving the use of caustic soda gives very accurate results when all the precautions described by Lasne are duly observed. The results obtained by Gruber's method, a simplification of the preceding, are inexact. Gladding's method only differs in detail from that of Lasne, caustic potash being substituted for caustic soda. The method of direct precipitation by ammonia, as carried out by Thomson, gives variable results, according to the nature of the phosphate under examination, and the precipitate always contains lime.

N. L.

**Technical Examination of Ferruginous Pigments.** By H. BAUCKE (*Zeit. anal. Chem.*, 1898, 37, 668—679).—The ferruginous pigments prepared by roasting ochres exhibit a gradation of shades ranging from yellowish-brown to deep purple, the depth of colour increasing with the temperature and duration of the roasting. Even in the most strongly heated specimens, the ferric oxide is practically all

soluble in concentrated hydrochloric acid, and digestion with that acid furnishes the most convenient means of dissolving the iron for estimation. The specific gravity of the substance increases with the depth of colour, being 3.484 in those most feebly roasted, and 4.462 in those most strongly heated; the passage from pale brown to red is accompanied by the most marked increase in specific gravity. As these pigments are largely used for painting iron-work, especially on railways, the degree in which they resist the action of the acids in coal smoke is of importance. The degree of resistance increases with the temperature of roasting, and comparative experiments on this point may conveniently be made by boiling the samples with excess of 1 per cent. sulphuric acid for a determined time (1 hour). The percentage of the total iron dissolved by this method is quite independent of the size of the particles, fractions exhibiting, under the microscope, diameters of 4—10  $\mu$ , giving up to the acid the same percentage as those of 30  $\mu$  and higher.

M. J. S.

**Analysis of Molybdenum Compounds.** By HARRY BREARLEY (*Chem. News*, 1898, 78, 203—205).—Chatard's process for the estimation of molybdenum by precipitation with lead acetate is accurate in neutral solution, but even if the solution is faintly alkaline decomposition of any excess of lead acetate ensues with deleterious effects; in the presence of 2 c.c. of free 33 per cent. acetic acid per 250 c.c., the results again are accurate, whereas with more free acid the precipitate loses its granular character, becomes powdery, and liable to pass through the filter. Excess of lead acetate may be detrimental in neutral or alkaline solutions, but is not so in acid solutions; in fact, water slightly acidified with acetic acid and holding, per litre, 2 c.c. of a solution of lead acetate (containing 7.896 grams per litre) may be used towards the end of a washing with pure hot water to prevent the formation of opalescent filtrates. To ignite the precipitate, it need not be removed from the paper, but the whole may be folded wet and dried in a crucible in the front of a muffle; ignition should be started at as low a temperature as possible to prevent the formation of imperfectly decarbonised patches that would require a dangerously high temperature to burn away; lead molybdate may, however, be exposed for hours at a temperature between 850° and 900° without suffering a greater loss than 1 per cent. The result is, moreover, either not affected at all, or, at any rate, not beyond + or - 1 per cent., by the presence of 0.1 or 0.2 gram of the following substances: sodium chloride or nitrate; ammonium chloride, nitrate, or acetate; manganese; copper; cobalt; nickel; zinc; magnesium; mercuric mercury; but uranium causes a difference of 1.7 or 1.5 per cent. The presence of ammonium acetate makes the precipitate powdery; copper and manganese darken the ignited precipitate, although the colour can be nearly removed by treatment with nitric acid and lead peroxide. Cobalt renders the ignited precipitate greyish, and on dissolving in hydrochloric acid imparts a green colour to the solution which disappears on dilution; 0.00005 gram of cobalt can be detected by this reaction, which, moreover, may probably prove useful in colorimetrically indicating the amount of cobalt present in the grey precipitate of lead molybdate.

In this and some other instances, redissolving the ignited lead molybdate precipitate in dilute hydrochloric acid, neutralising with ammonia, acidifying with acetic acid, and treating with a few additional drops of lead acetate, suffices to furnish a practically pure precipitate of lead molybdate. In the presence of zinc, molybdenum causes a cloudiness in the neutralised solution, which may be disregarded where it forms a mere opalescence on adding the excess of acetic acid, otherwise, when neutralising the hydrochloric acid, the final portions should be got rid of by means of ammonium acetate. Nickel exhibits this clouding effect to a lesser degree, mercury and uranium to a more marked extent; but in these cases, too, the warm, acidified solution may be cleared by adding ammonium acetate. Uranium colours the ignited precipitate yellowish-brown, and although it dissolves in hydrochloric acid, it needs repeated reprecipitations to remove the last traces of uranium from the lead molybdate.

Molybdenum may be estimated volumetrically by adding an excess of lead acetate, filtering off the lead molybdate, and determining the lead in the filtrate, or by Schindler's process, in which lead acetate is added to an acidified solution of a molybdate, until the latter ceases to give any coloration when mixed with tannin in a white cupped tile. This process is rapid, and gives approximate results; it may, however, be advantageously supplemented by filtering some of the liquid after the completion of the tannin reaction, and testing it, first with lead acetate, and, if necessary, with sodium molybdate; the intensity of any cloudiness indicates approximately the quantity of any unprecipitated molybdate or excess of lead, as the case may be, inasmuch as lead acetate gives a distinct cloudiness in solutions faintly but decidedly acid with acetic acid if they contain even as little as 1 part of molybdenum per 4,000,000.

D. A. L.

**Testing Otto of Roses.** By P. N. RAIKOW (*Chem. Zeit.*, 1898, 22, 523—524).—The author, in reply to Dietze (*Süddeutsche Apoth. Zeit.*, 1898, 174), states that the saponification number of the oil is but insignificantly increased when the sample has been previously filtered at 18°. As regards the solidifying point, he asks whether Dietze regards 15° or 20° as the limit of temperature.

An analysis is given of a sample which was undoubtedly genuine, but which would not satisfy Dietze's requirements: sp. gr. 0.855 at 27°/17.5°. Solidifying point, 20.5°; optical activity in a 100 mm. tube, 2° 45' at 25°; acidity figure, 1.1; saponification number, 15.5; ether number, 14.4; and relation figure (*Verhältnisszahl*), 13.

L. DE K.

**Detection and Estimation of Methylic Alcohol in Ethylic Alcohol.** By AUGUSTE TRILLAT (*Compt. rend.*, 1898, 127, 232—234).—When ethylic alcohol is oxidised with chromic mixture, it yields aldehyde, acetic acid, and acetal, whereas methylic alcohol, under the same conditions, yields acetic acid and methylal. When condensed with dimethylaniline, acetal yields the compound  $\text{CHMe}(\text{C}_6\text{H}_4\cdot\text{NMe})_2$ , which has not previously been described, and methylal yields tetramethyldiamidodiphenylmethane,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , and this, when oxidised, gives an intense blue coloration, permanent when the liquid

is heated. The acetal derivative, under the same conditions, yields an unstable blue compound which is decomposed on heating. When applying these facts to the detection of methylic alcohol in ethylic alcohol, precautions are necessary, because dimethylaniline often contains small quantities of methylic alcohol, and even of the base derived from methane, and also, when heated with certain acids in presence of air, it develops a blue coloration.

Twenty c.c. of the alcohol to be examined is diluted with 300 c.c. of water containing 30 grams of potassium dichromate in solution, and 100 c.c. of dilute sulphuric acid (1:5) is added. After standing for an hour at the ordinary temperature, the liquid is distilled, the first portions of the distillate being rejected, and the distillate is exactly neutralised with sodium hydroxide and redistilled almost to dryness. The second distillate is diluted to 400 c.c., and 100 c.c. is mixed with 2 c.c. of pure dimethylaniline and 1 c.c. of dilute sulphuric acid (1:10) and heated at 65—70° for 5 hours out of contact with the air. The liquid is made alkaline, the excess of dimethylaniline expelled by means of a current of steam, and the liquid, or part of it, acidified with acetic acid and mixed with lead peroxide suspended in water. The intensity of the blue colour produced is compared with that obtained with alcohol containing known percentages of methylic alcohol. It is well to make a blank experiment with pure ethylic alcohol.

C. H. B.

**Estimation of Glycerol in Sweet Wines.** By GUIDO FABRIS (*L'Orosi*, 1897, 20, 260—267).—The estimation of glycerol in wines containing much sugar presents special difficulties, and in the methods generally employed there is a loss of glycerol, which is not compensated for by the traces of sugar, colouring matter, &c., which are weighed with the latter. The German official method and that of Lecco, both of which involve the use of lime, give satisfactory results when certain precautions are observed; the following method of procedure is recommended.

Fifty c.c. of the wine is mixed with 5 grams of sand and 8—10 grams of calcium hydroxide, and the mixture evaporated to the consistency of a thin paste, which is then ground in a mortar and repeatedly extracted with hot alcohol of 96°, using 30—40 c.c. at each extraction. The filtered extract, which should amount to about 200 c.c., is evaporated to a syrupy consistence, and 10 c.c. of absolute alcohol and 15 c.c. of anhydrous ether gradually added; when the precipitate has subsided, the liquid is filtered, the filter washed with a mixture of alcohol and ether (2:3 vols.), the filtrate evaporated, and the residue dried for 1 hour at 100° and weighed. If the residue appears to be impure, it is redissolved in a mixture of 5 c.c. of alcohol with 7.5 c.c. of ether, filtered, evaporated, dried for half an hour at 100°, and weighed. Should more than 0.5 per cent. of glycerol be found, it is well to repeat the analysis with a smaller amount of the wine, so that the glycerol finally weighed may not exceed 0.3 gram. The isolation of larger quantities of glycerol is found to be accompanied by a more than proportionately greater loss.

N. L.

**Nitration of Glycerol with Nitrous Acids.** By R. AUZENAT (*Chem. News*, 1898, 78, 258—259).—Glycerol, of sp. gr. = 1.262, was treated with 97 per cent. sulphuric acid and 94 per cent. nitric acid containing varying proportions of nitric peroxide. The nitroglycerols obtained were washed in the ordinary way with water, and, in addition, twice at 60° with equal volumes of a 4 per cent. solution of sodium carbonate, the alkali being finally removed with distilled water. These products were filtered and submitted to the heat test, and it was found that nitroglycerol satisfying this test can be prepared with nitric acid containing as much as 3 per cent. of nitric peroxide, although decomposition during the nitration frequently occurs with anything above 2 per cent. The presence of free sulphuric acid is not detected by the heat-test, although it is dangerous if the explosive has to be stored, but the test is effective in rejecting any nitroglycerol containing more than 0.003 per cent. of free nitric acid. Washing with sodium carbonate at a high temperature increases the stability. D. A. L.

**Detection of Acetone.** By PASQUALE MALERBA (*Zeit. anal. Chem.*, 1898, 37, 690; from *Ann. Chim. Farm.*, 21, 14).—On adding, drop by drop, a 1—2 per cent. solution of dimethylparaphenylenediamine to the suspected liquid, a red coloration gradually appears, and increases in intensity after some hours. Both alkalis and strong mineral acids change this colour to a bright violet. M. J. S.

**Estimation of Formic Acid in the Presence of Acetic Acid and of Easily Oxidisable Substances.** By ALEXANDER LEYS (*Chem. News*, 1898, 78, 245—246).—When acetic acid containing formic acid is mixed with mercuric acetate, crystalline mercurous acetate forms in proportions exactly corresponding to the quantity of formic acid present. Dilute, 1 per cent., solutions are best for the reaction, which takes place at the ordinary temperature, but is expedited by heating, and is complete at the boiling point; it is, moreover, not affected by the presence of alcohol, acetic acid, or aldehyde. To estimate formic acid, the total acidity of the solution is first ascertained, and if much acetic acid is present, the solution is diluted to 20 or 30 per cent.; if, however, the proportion of formic acid to acetic acid is 1 to 20, or greater, the solution is diluted to 2 per cent. acidity. Ten c.c. of this is mixed with 20—30 c.c. of a 20 per cent. solution of mercuric acetate, and made up to 100; it is heated during 7 or 8 minutes up to the boiling point and allowed to cool overnight. The precipitate is collected on a glass wool filter, washed 4 or 5 times with alcohol of 95° containing 2 per cent. of glacial acetic acid, then 2 or 3 times with neutral alcohol of 95°, finally with dry ether to remove the alcohol. It is dried in the air or in a vacuum, dissolved in nitric acid diluted with an equal volume of water, mixed with sodium chloride and the mercurous chloride filtered, washed, dried at 100°, and weighed; the number obtained, multiplied by 0.0976, gives the corresponding weight of formic acid.

In mixtures of formic acid and alcohol, or of formic acid, alcohol

and acetic acid in which the latter is not present in sufficient quantity, 2 c.c. of glacial acetic acid is added before the mercuric acetate.

D. A. L.

**Estimation of Potassium Hydrogen Tartrate in Wines.** By HENRY JAY (*Bull. Soc. Chim.*, 1897, [iii], 17, 626—629).—The author has examined both Berthelot and de Fleurieu's and Reboul's methods for estimating potassium hydrogen tartrate in wines. The former, which depends on the precipitation of the salt by the aid of alcohol, gives numbers somewhat too low, but may be rendered more accurate by suitable corrections. The results obtained by Reboul's method, which depends on evaporating down the wine and crystallising the salt, are much too high, as malates, &c., are also carried down with the tartrate.

J. J. S.

**Microchemical Reactions.** By CONSTANTIN SAINT-HILAIRE (*Zeit. physiol. Chem.*, 1898, 26, 102—109).—In order to test microchemically for uric acid, the sections obtained from organs hardened in alcohol, and embedded in celloidin, are placed in a 5 to 10 per cent. solution of copper sulphate for some hours; the compound which uric acid forms with copper is then reduced by placing the sections for a few minutes in a boiling saturated solution of sodium hydrogen sulphite; after washing, the sections are finally treated with potassium ferrocyanide; concretions of uric acid are by this means coloured red.

In some preparations, the chromatin network of the nuclei was observed to be somewhat similarly stained, and it was found that the alloxuric bases, histon and protamine, are similarly affected. The constituent of the nucleus which gives the reaction is believed to be histon, combined as nucleo-histon.

W. D. H.

**Examination of Beeswax.** By KARL DIETERICH (*Zeit. anal. Chem.*, 1898, 37, 699—700; from *Helfenberger Annalen*, 1897, 218), and by GEORG BUCHNER (*ibid.*, 700; from *Zeit. öffent. Chem.*, 1897, 3, 570).—For the estimation of the "saponification number" of a glyceride, it is recommended by Henriques to dissolve 3—4 grams of the substance in 25 c.c. of light petroleum, add an excess of alcoholic soda, and allow to remain in the cold until the next day; saponification is complete, and the results of this "cold saponification process" agree absolutely with those of saponification by heat, whilst, in some cases, such as mixtures of beeswax and ceresin, cold saponification is even more satisfactory than the usual method, provided that a petroleum is selected in which the substance is perfectly soluble. The author maintains that, with beeswax, cold saponification gives lower values than the hot method, and that the saponification number is more affected than the acid number.

BUCHNER ascribes these differences to the use of a petroleum having too low a boiling point (55—75° instead of 100—150°).

M. J. S.

**New Colour Reaction for Phenylhydrazine.** By LOUIS SIMON (*Compt. rend.*, 1898, 126, 483—485).—The addition of a few drops of an aqueous solution of sodium nitroprusside to a warm solution of phenylhydrazine and trimethylamine develops a blue

coloration, the intensity of which is increased by subsequently adding a concentrated solution of potash. The coloration, although fugitive, is very intense, and serves to detect 1 part of phenylhydrazine in 50,000. The presence of alcohol, ether, or ammonia, is not detrimental, but chloroform, benzene, and acids hinder the production of the colour, whilst acetone gives its own characteristic red coloration. This reaction is limited to phenylhydrazine and to those derivatives which, like orthotolylhydrazine and 1:4-bromophenylhydrazine, are substituted in the aromatic nucleus; alkylic and acylyl derivatives of phenylhydrazine, hydrazones, semicarbazide, and hydrazine hydrate, under similar conditions, give no colour reactions of this nature.

G. T. M.

**Estimation of Caffeine in Coffee.** By E. TASSILLY (*Bull. Soc. Chim.*, 1897, [iii], 17, 761—766 and 766—768).—The methods employed for the estimation of caffeine in coffee may be classed in three groups. 1. The coffee, with or without the addition of lime, magnesia, or ammonia, is extracted with warm chloroform. 2. The coffee is extracted with hot water and the solution shaken with chloroform, either directly or after evaporation with magnesia. 3. The coffee, with or without the addition of an alkali, is treated with a solution of sodium benzoate (Herlant) or salicylate (Gorges) and the liquid then extracted with chloroform. The methods of the first group give uncertain results, with the exception of that of Grandval and Lajoux, in which ammonia and ether are employed. Of the methods of the second group, those of Dvorkovitch and of Domergue and Nicolas give satisfactory results, and may be employed when time does not allow the use of the more accurate, but tedious, processes of Herlant and Gorges.

Since the complete desiccation of hydrated caffeine is somewhat troublesome, it is always preferable to weigh it after crystallisation from chloroform. In order to obtain a pure product, it is necessary to use an alkali in the extraction, and magnesia is to be preferred to lime, since the latter, in presence of water at 100°, causes decomposition of caffeine with liberation of ammonia. Some other slight modifications in the working of the various processes are suggested.

In the second paper, the author describes a new process, which is carried out as follows. Ten grams of the powdered sample is extracted five times with boiling water, 200 c.c. of the latter being used for each extraction. Half of the liquid thus obtained is evaporated to dryness, the residue made into a paste with 1—2 c.c. of 10 per cent. sulphuric acid, and thoroughly extracted with boiling water. The aqueous extract is then either (1) evaporated to dryness with 20 grams of sand and 2 grams of magnesia, and the caffeine extracted by digestion with warm chloroform, or (2) made alkaline with ammonia and repeatedly agitated with chloroform in the cold. The best results are obtained by the second mode of procedure, and the test analyses quoted are very satisfactory.

N. L.

**Artificial Coloration of Coffee.** By GIULIO MORPURGO (*L'Orosi*, 1897, 20, 397—403).—With the object of improving its appearance, coffee is frequently subjected to the processes of (1) washing with



water to which antiseptics, such as boric acid, are often added; (2) colouring with mixtures of various substances, of which the most commonly used are graphite, bone black, soot, ultramarine, Berlin blue, lead chromate, iron tannate, yellow ochre, chalk, talc, and various aniline colours; (3) polishing with resin, wax, sandarach, talc, and similar substances.

The colour of the sample and its appearance when examined with a lens often afford indications of the treatment to which it has been subjected. The presence of resin is shown by the turbidity produced on adding water to the cold alcoholic extract. Wax may be extracted by heating with alcohol to which a little ether has been added. For the detection of colouring matters, 50 grams of the coffee is boiled for half an hour, first with alcohol alone, and then with alcohol rendered slightly alkaline with potash, and after the filtrates have been allowed to stand for some hours, the sediment is examined by microchemical methods. The treatment with alkaline alcohol removes those colouring matters, such as carbon and lead chromate, which adhere more closely to the seed. The lighter particles of vegetable matter may be separated by treating the sediment with chloroform and allowing the liquid to stand for 24 hours. N. L.

**Method for Testing Natural and Artificial Organic Colours.** By A. G. ROTA (*Chem. Zeit.*, 1898, ii, 437—442).—The author has tabulated a scheme for the detection of organic dyes and separation of the same.

The chief reagent used is stannous chloride containing free hydrochloric acid, which reduces some colouring matters, but does not affect others. The separation of the colours is effected by ether, either in acid, neutral, or alkaline solution. Wool is also used to separate basic colours from acid compounds. L. DE K.

**Detection of Elderberry Juice in Extract of Ergot.** By ITALO CEPPELLINI (*L'Orosi*, 1898, 21, 47—48).—About 1 gram of the suspected extract is dissolved in 6 c.c. of water acidified with 30 drops of concentrated sulphuric acid, and the solution vigorously shaken with 10 c.c. of oil of turpentine; after half an hour, it is again shaken and passed through a filter previously moistened with oil of turpentine. If the extract is pure, the aqueous layer acquires the colour of sherry, whilst the oily layer remains colourless. If, however, not less than 10 per cent. of elderberry juice is present, the oil of turpentine acquires a more or less intense yellowish-green tint, and the aqueous layer is of a fuller wine-red colour. N. L.

**Estimation of Tannin.** By LÉO VIGNON (*Compt. rend.*, 1898, 127, 369—372).—Silk free from gum absorbs tannin readily and completely from solutions of tanning materials at 50°, but does not absorb gallic acid, glucose, &c. About 5 grams of silk is necessary for 0.1 gram of tannin dissolved in 100 c.c. of water. The tannin may be estimated by (a) the increase in the weight of the silk, (b) the difference in the proportion of solid matter in the solution before and after the treatment with silk, (c) by titration with permanganate. The last method is the most exact, but b is simple and expeditious, and gives results sufficiently exact for practical purposes.

The silk is prepared by boiling 20 grams of raw silk for 30 minutes with a solution of 50 grams of white soap dissolved in 500 c.c. of water, this treatment being repeated and the silk then well washed.

The tannin solution is prepared by treating in the usual way from 10 to 20 grams of the tanning material. One thousand c.c. of the solution should contain about 3 grams of tannin. Twenty-five c.c. of this solution is diluted to 250 c.c., and 100 c.c. of the diluted liquid is heated at 50° for 5 hours, but not more, with 5 grams of the prepared silk. Titration with permanganate and indigo, before and after the treatment with silk, is conducted in the usual way.

The results with sumach and oak galls are practically identical with those obtained by precipitating the tannin with cat-gut or ammoniacal zinc acetate, and the method is more expeditious. The special reagent (silk) is very readily prepared and is practically constant in composition.

C. H. B.

**A New Proteid Reaction.** By J. H. ELLIOTT (*J. Physiol.*, 1898, 23, 296—300).—Dilute [sulphuric acid (1 to 5 of water) acting on proteids produces a bluish-violet coloration when allowed to concentrate slowly. When the proteid matter is digested, the colour passes into the liquid; this shows a wide absorption band reaching from *C* to *E* or *b*.

The test may be employed microchemically. The colour disappears from sections when they are transferred from acid to water, alcohol, or saline solutions, and returns on placing them (even after 3 weeks) again in the acid, or in strong solutions of nitric or hydrochloric acids. Deposits of lardacein are shown very distinctly by this method.

W. D. H.

**Separation of Albumoses from Peptone.** By PAUL MÜLLER (*Zeit. physiol. Chem.*, 1898, 26, 48—55).—The method suggested, which is stated to have advantages over Kühne's ammonium sulphate process, is a modification of that originally introduced by Schmidt-Mulheim.

To the solution, an equal volume of 30 per cent. ferric chloride solution is added, and then alkali until the reaction is only feebly acid. The voluminous precipitate is filtered off, and to the filtrate a pinch or two of zinc carbonate is added, the mixture shaken and again filtered. The final filtrate is free from albumoses.

If leucine and tyrosine are present, small quantities of these substances are carried down with the precipitate.

W. D. H.

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## General and Physical Chemistry.

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**Dissociation-spectra of Fused Chlorides, Bromides, and Iodides.** By ARNAUD DE GRAMONT (*Bull. Soc. Chim.*, 1897, [iii], 17, 897—898, 899—900, 900—901).—The author has examined the spark-spectra of the chlorides of sodium, lithium, potassium, rubidium, cadmium, and zinc, the bromides of sodium, potassium, calcium, and zinc, and the iodides of sodium, potassium, and cadmium, and finds that they exhibit the chief lines of the spark-spectrum of the halogen present; detailed measurements are given in the paper, and the method can be used for the detection of minute traces of the halogens.

T. M. L.

**Single Differences of Potential.** By HECTOR R. CARVETH (*J. Physical Chem.*, 1898, 2, 289—321).—The author has determined a number of single differences of potential by the dropping mercury method, attention being directed more especially to the measurement of metals in solutions of their salts; in opposition to the results of Paschen, it would appear that both anion and cation have an effect. With different concentrations of the same electrolyte, the values obtained apparently follow in regular order. Cases in which the dropping electrode gives values corresponding with the polarisation method have been observed, as well as cases in which a difference in the values occurs. The solution pressure formula of Nernst was tested, and found to hold approximately in a few cases, whilst in the great majority of cases it failed. The author concludes that the values given by the drop electrodes are not true single differences of potential.

H. C.

**Transference Number for Hydrogen.** By DOUGLAS MCINTOSH (*J. Physical Chem.*, 1898, 2, 273—288).—The author, after attempting to determine the transference numbers for hydrogen in different acids by the Helmholtz method, using gas electrodes, comes to the conclusion that the method is not applicable to gas cells. It is probable that the source of error is to be found in the solubility of the electrode in the electrolytic solution. The results indicate that the transference number for hydrogen in hydrochloric acid does not change with the dilution between normal and thousandth-normal solutions.

H. C.

**Influence of Pressure on the Electrical Conductivity of Solutions.** By A. BOGOJAWLENSKY and GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1898, 27, 457—473).—The influence of pressure is due to the changes produced in (1) volume, (2) viscosity, (3) degree of dissociation, (4) dissociation of the solvent, and is given by the equation  $1/\lambda \times d\lambda/dp = 1/v \times dv/dp + 1/\eta \times d\eta/dp + 1/a \times da/dp + \lambda_1/\lambda a_1 \times da_1/dp$ . The last term may be neglected if the number of ions of the solute far exceeds that of the solvent ions. The volume changes of aqueous solutions have been calculated in previous papers, and the first partial value is obtainable. From Cohen's determinations of the effect of pressure on

viscosity, the values  $1/\eta \times d\eta/dp$  are also obtainable for sodium chloride solutions. The effect of pressure on the dissociation constant is given by the expression  $d \log. k/dp = -\Delta v/1000RT$ , where  $\Delta v$  is the volume change (which must be expressed as a function of the pressure) consequent on the dissociation of a gram-molecule of the solute. The values  $1/a \times da/dp$  are hence obtained, and from the sum of the three partial values the total pressure effects are calculated for pressures of 100, 200, 300, 400, and 500 atmospheres. The variation of the pressure effect with varying degrees of dissociation is seen in the case of the chlorinated acetic acids; the values for  $1/\lambda \times d\lambda/dp$  decrease with increase of dissociation, and are in all cases in good accord with the values found. In the cases of aqueous solutions of ammonia and water, the volume changes consequent on dissociation are unusually great, hence also the conductivity change due to pressure; in the case of ammoniacal solutions the found and calculated values are compared, with fair agreement. For very dilute solutions, the dissociation of the solvent becomes important, and this is allowed for in the case of dilute solutions ( $v=500$  to  $v=50,000$ ) of hydrogen and sodium chlorides; the pressure effect is found to increase rapidly with dilution, but not as rapidly as calculated. The apparatus employed for the determination of conductivity at high pressures is described, and the results of the determinations are given, the compounds examined being solutions of acetic, monochloroacetic, dichloroacetic, trichloroacetic, phosphoric, citric, tartaric, benzenesulphonic, and hydroferrocyanic acids, sodium phosphate, tartrate, and chloride, potassium citrate and ferrocyanide, and ammonia.

L. M. J.

**Thermal Equilibrium in Electrolysis.** By DONATO TOMMASI (*J. Physical Chem.*, 1898, 2, 229—232).—A compound capable of being oxidised or reduced is submitted to the simultaneous action of an oxidising and a reducing agent. This is effected by making use of the mixture of hydrogen and oxygen obtained by the electrolysis of water containing in solution the compound under examination. The platinum electrodes are brought as closely together as possible, the liquid is frequently stirred, and the current reversed occasionally. The following results were obtained.

Initial compound.	Final compound.
Nitric acid.	Ammonia and nitrite.
Potassium nitrate.	„ „
Sodium nitrate.	„ „
Potassium nitrite.	Ammonia.
Potassium chlorate.	Perchlorate.
Arsenic acid.	No change.
Potassium arsenate.	„ „
Arsenious acid.	Arsenic acid.
Potassium arsenite.	Arsenate.
Ferrous sulphate.	Partial oxidation.
Ferric sulphate.	Partial reduction.

From these experiments, the author deduces the following laws.

1. When a substance is submitted to two equal and contrary

chemical actions, the reaction which develops the most heat will take place in preference, provided always that it can begin.

2. Of two chemical actions, that which requires less heat to start it will always take place in preference, even if it develops less heat than the other action.

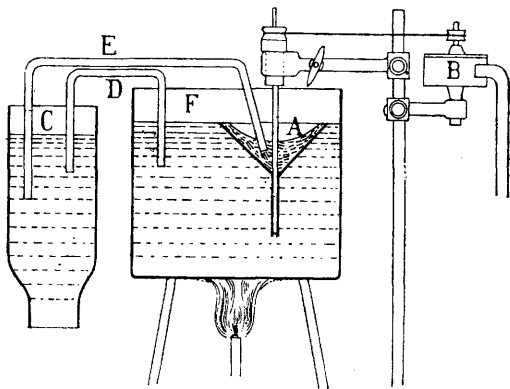
H. C.

**Magnetic Rotation in Salt Solutions.** By S. OPPENHEIMER (*Zeit. physikal. Chem.*, 1898, 27, 447—456).—It has been shown by Perkin (*Trans.*, 1889, 680; 1894, 20) and by Schönrock (*Abstr.*, 1895, ii, 196) that the magnetic rotation of solutions of hydrogen chloride decreases with increase of concentration, and the author, therefore, endeavoured to determine whether the same effect could be observed with salt solutions if sufficiently sensitive instruments were used. The half-shadow apparatus used by Schönrock with a polarisation tube 80 cm. long was employed, and solutions of sodium and potassium chlorides and bromides, cadmium chloride, and acetic acid were examined, but in no case was any effect of concentration apparent.

L. M. J.

**Constant Temperature Device.** By HAMILTON P. CADY (*J. Physical Chem.*, 1898, 2, 242—244).—In order to keep a constant temperature in an apparatus which cannot be immersed in a bath, water having a constant temperature may be circulated round the apparatus by the device illustrated in the cut. A is an ordinary

75 mm. glass funnel mounted on a glass rod and running in the bearings of a Witt stirrer. F is a large water-bath kept at the desired temperature. C is the apparatus through which the water is to circulate. The siphon D connects C and F, so that the water comes to the same level in both vessels. A is adjusted so that the top



of the funnel comes just at the surface of the water in F. The siphon E connects the interior of the funnel with C, so that when equilibrium is reached the level of the liquid in A, F, and C is the same. If A is caused to rotate, the water in A will be thrown out, and the level of the liquid will be lower than that in C. This will cause water to flow through E from C to A, and back again through D from F to C. This will set up a circulation of water through C which will continue as long as A is rotated.

H. C.

**Experimenting at Low Temperatures.** By WALTHER HEMPEL (*Ber.*, 1898, 31, 2993—2997).—A test-tube 4 cm. wide was placed in a beaker 13 cm. wide, and the intermediate space packed with some

non-conducting material. This apparatus was compared with a Dewar's tube, of which the inner vessel had the same dimensions as the test-tube; equal quantities of solid carbonic anhydride and ether were placed in each, and the temperature read at intervals by means of an electropymeter. It was found that, with a packing either of eider-down or of pure wool dried at  $100^{\circ}$ , cooling was prevented almost as well as with the best-exhausted Dewar's tubes, and better than with the ordinary commercial ones. A packing of dry wool should, then, be placed round vessels in which ice or a freezing-mixture is kept, and filters in which it is desired to filter at a low temperature should be similarly packed; the filter may be a double one, with the space between filled with solid carbonic anhydride and ether.

For collecting solid carbonic anhydride, a cardboard funnel is recommended, with a very short neck closed with a cork, and an annular strip of linen fastened round the edge of the funnel so as to form a bag. The cylinder of liquid anhydride is placed mouth downwards in a slanting position; the linen bag is grasped with the gloved hand and gathered round the mouth of the cylinder, which is then opened; solid anhydride collects in the bag, and may be shaken down through the neck into a suitable receptacle. From 1 kilo. of the liquid anhydride, 270—300 grams of the solid can be obtained; at the prices current in Germany for the liquid, the solid thus costs 2s. per kilo. The lowest temperature (about  $-79^{\circ}$ ) is attained by mixing the solid anhydride with so much ether that not too stiff a magma is formed; the temperature then remains constant so long as solid particles are still present.

C. F. B.

**Boiling Point Curve for Benzene and Alcohol.** By E. F. THAYER (*J. Physical Chem.*, 1898, 2, 382—384).—The following table gives the percentage of benzene in the solutions examined, the boiling points, and the corresponding barometric readings in millimetres of mercury.

Benzene.	Temp.	Bar.	Benzene.	Temp.	Bar.
100.00	79.5°	736.9	67.15	66.9°	735.8
95.18	70.8	728.5	59.21	67.1	735.3
93.87	69.6	728.5	44.45	67.5	732.9
92.64	68.8	728.5	35.11	68.4	732.9
85.28	67.6	736.3	27.14	69.8	732.9
76.00	67.1	736.0	15.86	72.1	732.9

The first addition of alcohol to benzene lowers the boiling point a great deal; then comes a nearly horizontal curve followed by a rise at the alcohol end which is somewhat less steep than at the benzene end.

H. C.

**Boiling Point of Mixed Solutions. I.** By THEODORE W. RICHARDS and WENTWORTH LEWIS HARRINGTON (*Zeit. physikal. Chem.*, 1898, 27, 421—425).—By the addition of a gram-molecule of cadmium oxalate to 10 litres of water containing a slight excess of hydrogen chloride, the boiling point is depressed to the extent of  $0.101^{\circ}$ . This is explained by the formation of two almost undissociated molecules, namely, cadmium chloride and oxalic acid, thus  $2\text{H}' + 2\text{Cl}' + \text{CdC}_2\text{O}_4 =$

$\text{CdCl}_2 + \text{H}_2\text{C}_2\text{O}_4$ . From the known dissociation of the hydrochloric acid, on the assumption that there is no dissociation in the products, the number of molecules removed is calculated as 1.6, hence the depression =  $0.083^\circ$ , whilst from the known effects of hydrochloric acid, cadmium chloride, and oxalic acid on the boiling point of water, the depression is calculated as  $0.093^\circ$ , both results being lower than that actually obtained. Analogous results were obtained by the use of cadmium citrate, the calculated depression being  $0.364^\circ$ , whilst the value found was  $0.434^\circ$ .

II. By CLARENCE M. C. GORDON, L. J. HENDERSON, and W. L. HARRINGTON (*ibid.*, 425—428).—Experiments similar to the preceding were made with sodium chloride and cadmium sulphate; in this case, also, a depression of the boiling point occurs, owing to the dissociation of sodium sulphate being less than that of sodium chloride. The greatest possible decrease of molecular groups is given by  $\text{CdSO}_4 + 2(1 - \alpha)\text{NaCl} + 2\alpha\text{Na}' + 2\alpha\text{Cl}' = \text{CdCl}_2 + \text{Na}_2\text{SO}_4$ , that is,  $= 2\alpha$ . From the known dissociation of sodium chloride, the maximum depressions (that is, for undissociated sodium sulphate) in the cases examined are  $0.081^\circ$  and  $0.036^\circ$ , whilst those found were  $0.093^\circ$  and  $0.060^\circ$ . From this, it appears that either the accepted dissociation values are incorrect, or that even in dilute solutions of cadmium salts double molecules occur.

L. M. J.

**Study of a Three-Component System.** By HECTOR R. CARVETH (*J. Physical Chem.*, 1898, 2, 209—228).—Numerous determinations were made of the freezing points of mixtures of the nitrates of lithium, sodium, and potassium, the results being plotted on the triangular diagram (*Abstr.*, 1898, ii, 65). The composition and melting points of the three binary and the ternary eutectic mixtures are approximately as follows.

Percentage composition.			M. p.
$\text{LiNO}_3$	$\text{NaNO}_3$	$\text{KNO}_3$	
47	53	—	204°
34	—	66	129
—	45.5	54.5	218
30	14	56	120

H. C.

**Thermochemistry of Sodium Suboxide and Peroxide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1898, 127, 514—516).—The reaction  $\text{Na}_2\text{O sol.} + 2\text{H}_2\text{O liq.} + \text{Aq} = 3\text{NaOH diss.} + \text{H gas}$  develops + 97.78 Cal., hence  $\text{Na}_3\text{ sol.} + \text{O gas} = \text{Na}_3\text{O sol.}$  develops + 101.57 Cal. or + 67.62 Cal. for  $\text{Na}_2$ .

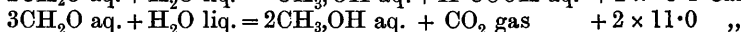
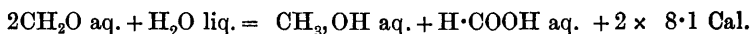
The reaction,  $\text{Na}_2\text{O}_2\text{ sol.} + 2\text{HCl diss.} = 2\text{NaCl diss.} + \text{H}_2\text{O}_2\text{ diss.}$  develops + 41.81 Cal., hence  $\text{Na}_2\text{ sol.} + \text{O}_2\text{ gas} = \text{Na}_2\text{O}_2\text{ sol.}$  develops + 119.79 Cal. The heat of formation of the monoxide is about 100 Cal.

The rapidity of the action of water and other reagents on the

suboxide is partly attributable to the large area of its surface resulting from its porous character. C. H. B.

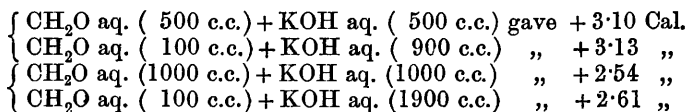
**Heats of Formation of Cyanic Acid and Carbamide.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1897, [vii], 11, 145—149).—This paper gives details of thermochemical determinations previously recorded (Abstr., 1897, ii, 7). G. T. M.

**Thermochemistry of Formaldehyde.** By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1897, [iii], 17, 849—859. Compare Abstr., 1897, ii, 359).—The author recognises two polymeric modifications of formaldehyde, namely, trioxymethylene or metaformaldehyde,  $(\text{CH}_2\text{O})_n$ , produced by the polymerisation of anhydrous formaldehyde, and by the action of dehydrating agents on the concentrated aqueous solution; and paraformaldehyde produced on evaporating the aqueous solution. Paraformaldehyde is distinguished from metaformaldehyde by its solubility in water; it is invariably hydrated (compare Lösekann, Abstr., 1892, 423), and is regarded by the author as containing a number of compounds of the series  $(\text{CH}_2\text{O})_n \cdot \text{H}_2\text{O}$ , of which methylene glycol is the first member. It is now shown that the heat of formation of metaformaldehyde is identical with that of formaldehyde in aqueous solution, namely, 40.4 Cal.; as the heat of formation of the anhydrous substance is only 25.4 Cal. there is a development of heat = 15.0 Cal. in the polymerisation, which is, therefore, a strongly exothermic action. The dissolution of metaformaldehyde, which takes place when it is heated with water at 130° in sealed tubes, is an isothermic action, but two exothermic changes also occur,



for this reason, formaldehyde is a methylating agent of greater power than methylic alcohol. The heat of formation of a specimen of paraformaldehyde, of the composition  $\text{CH}_2\text{O} \cdot \frac{1}{3}\text{H}_2\text{O}$  was found to be 42.5 Cal.; this value is 2 units greater than that of metaformaldehyde, and serves to explain the fact that the latter is only produced from the aqueous solution in presence of dehydrating agents.

The action of potash on aqueous formaldehyde does not lead to the production of any definite compound, although heat is developed, especially in concentrated solution. The development of heat depends only on the final, and not on the initial, concentration of the solution; thus, for molecular proportions,



The heat of dilution of the potash solution is insignificant, and that of the formaldehyde must, therefore, be equally small; as, however, a sudden development of heat occurs on diluting a concentrated solution, the slow absorption of heat which follows must be of equal magnitude; for the first phase,  $\text{CH}_2\text{O aq. (100 c.c.)} + \text{H}_2\text{O (900 c.c.)}$  gave + 0.45 Cal. The slow absorption of heat corresponds with the



slow decrease of molecular weight observed by Grossman and Escheweiler (Abstr., 1890, 1092), and, in the opinion of the author, is due to the gradual dissociation of the paraformaldehyde in the solution. The first development of heat he regards as due to the hydration of monomolecular formaldehyde, and by cooling a 30 per cent. solution to  $-40^{\circ}$ , he was able to separate a solid hydrate, which melted between  $-30^{\circ}$  and  $-25^{\circ}$ , and had approximately the composition,  $\text{CH}_2\text{O} + 3\text{H}_2\text{O}$ .  
T. M. L.

**Thermochemistry of Isoamylmalonic Acid.** By GUSTAVE MASSOL (*Compt. rend.*, 1898, 127, 526—528).—Isoamylmalonic acid, prepared by the action of isoamylic iodide on ethylic sodiomalonate and crystallised from ether, forms anhydrous crystals which melt at  $98^{\circ}$ ; heat of dissolution,  $-2.50$  Cal.; heat of neutralisation by potassium hydroxide, 1st equivalent  $+13.90$  Cal.; 2nd equivalent  $+13.95$ ; total  $+27.85$  Cal. Heat of dissolution of the anhydrous potassium salt  $+6.44$  Cal., hence  $\text{C}_8\text{H}_{14}\text{O}_4$  sol.  $+2\text{KOH}$  sol.  $= \text{C}_8\text{H}_{12}\text{O}_4\text{K}$  sol.  $+2\text{H}_2\text{O}$  sol. develops  $+46.69$  Cal. The corresponding value for suberic acid is  $+44.76$  Cal., hence the value of the acidic function is higher for isoamylmalonic acid than for suberic acid, a result which affords additional evidence in support of the conclusion previously arrived at that in the oxalic series the thermal value of the acidic function of the normal acid is lower than the corresponding value for its isomerides, and is always related to the degree of separation of the two carboxyl groups.  
C. H. B.

**Solution of Solids and Liquids in Gases.** By P. VILLARD (*Chem. News*, 1898, 78, 297—298, 309—310. Compare Hannay and Hogarth, Abstr., 1880, 210; Pictet, 1895, ii, 201, and Villard, *ibid.*, 255).—At a temperature of  $17^{\circ}$ , gases under pressure take up considerable quantities of liquids and solids. Oxygen under 4 atmospheres absorbs an increased amount of bromine, which is still more marked at 50, 100, or 200 atmospheres. At 100 atmospheres, the density of the suspended bromine appears to be almost three times that of a saturated bromine atmosphere in a vacuum; the colour of the atmosphere under pressure is deeper than when no compression is employed, and when the pressure is released the bromine is deposited. Iodine also volatilises in compressed oxygen, but to a less extent than bromine, whilst air and hydrogen under pressure also sustain increased quantities of bromine.

Methane is very active in this direction; ethylic chloride at 180 atmospheres dissolves in 5 or 6 times its volume of methane, whilst at 200 atmospheres the two become miscible in any proportion and the surface of separation between the gas and the liquid disappears. The same phenomenon takes place with carbon bisulphide under about 550 atmospheres at the ordinary temperature, and under 250 atmospheres at  $150^{\circ}$ . Iodine, camphor, and paraffin also volatilise in compressed methane, and on releasing the pressure the iodine and camphor crystallise on the inside of the tube, and the paraffin falls out in brilliant flakes.

Ethylene under 300 atmospheres pressure takes up sufficient iodine to colour it a very deep violet, but in time the colour disappears as combination ensues. Compressed ethylene also dissolves paraffin,

stearic acid, and camphor ; the latter volatilises readily under small pressure, and when the pressure is increased to 150 atmospheres, the unvolatilised camphor becomes liquid, but continues volatilising as the pressure is further increased ; on releasing the pressure, the same phenomena ensue, but in the reverse order. Compressed nitrous oxide takes up bromine to the same extent at 20 atmospheres as oxygen at 40 and compressed carbonic anhydride takes up iodine, but the pressures that can be obtained are limited by the liquefaction of the gas. Critical point phenomena are observed in these experiments either when the temperature is raised and the pressure kept constant or *vice versâ*. It is suggested that these observations may find application for the distillation of substances that are decomposed by heat ; when taking up under pressure in a suitable gaseous medium and redepositing by relieving the pressure might in some cases prove more advantageous than distilling in a vacuum.

D. A. L.

**Solution Pressure of some Haloid Salts.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1898, 18, 327—330).—The solubility of the haloid salts of the alkali metals in alcohols decreases with rising molecular weight of the alcohol, and increases with rising molecular weight of the salt, the chlorides having the lowest and the iodides the greatest solubilities. In the case of the haloid salts of cadmium, copper, silver, mercury, and lead, the solubility also decreases with the rising molecular weight of the alcohol, but the iodides in these cases have the smallest and the chlorides the greatest solubilities.

H. C.

**Some Reactions in Methylic Alcohol and Acetone.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1898, 18, 322—326).—Methylic alcohol occupies a position, as a solvent, between that of water and ethylic alcohol. Ionisation takes place to a greater extent than in ethylic alcohol, and is in some cases even equal to that in water ; reactions, therefore, usually take place in methylic alcohol as in water. In acetone, ionisation does not take place to the same extent, and the reactions are, therefore, frequently modified. Mercuric iodide is far more soluble in acetone than in water, and potassium chloride is much less soluble ; consequently, in dilute solution in acetone, potassium iodide and mercuric chloride give a precipitate of potassium chloride. For similar reasons, potassium iodide and cadmium bromide give a precipitate of potassium bromide.

H. C.

**Benzene, Acetic Acid, and Water.** By JOHN WADDELL (*J. Physical Chem.*, 1898, 2, 233—241).—The distribution ratio of acetic acid in benzene and water as solvents was studied ; an exponential formula of the general form  $xy^n = \text{const.}$ , where  $x$  and  $y$  refer to the amounts of benzene and water in a constant quantity of acetic acid, is only found to give an approximate representation of the results. The ratio of acetic acid in water to acetic acid in benzene increases indefinitely with increasing dilution. The percentage of acetic acid in the aqueous phase passes through a maximum. The ratio of benzene to water in the more dense phase is greater than unity over a portion of the isothermal, even when the concentrations are expressed in reacting weights.

H. C.

**Equilibria of Stereoisomerides.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1898, 2, 143—158, and 245—255).—The theory of permanent changes developed by Duhem (Abstr., 1897, ii, 439), and applied by him to explain the behaviour of supercooled sulphur, is extended by the author to organic compounds which exist in isomeric modifications, such as stilbene dichloride, acetaldoxime, benzaldoxime, and others. In general, we have in these cases two modifications in equilibrium in the liquid phase, the presence of the one lowering the freezing point of the other. If we take into account the element of time, equilibrium may be reached practically instantaneously, or in a measurable length of time, or the system will appear to contain two components provided we act rapidly enough, and one component provided we act slowly. If a solid substance melts at one temperature and freezes at another, this is proof positive of the existence of two liquid modifications, provided no decomposition takes place. If the more fusible of two solid modifications is the more stable, we are also justified in deducing the existence of two liquid modifications, although the converse is not necessarily true, and if the less fusible of two solid modifications is the more stable, it does not follow that only one liquid modification is possible.

A discussion is also given of the conditions under which a reversal of stability does and does not take place, on adding another component which forms no compounds with the two modifications. H. C.

**Dissociation of Polyvalent Salts.** By PAUL CALAME (*Zeit. physikal. Chem.*, 1898, 27, 401—420).—The degrees of dissociation of a number of metallic salts of organic acids were determined at various dilutions, the ratio of the actual to the normal molecular depression being given. For formates and acetates, the values are almost identical; in the cases of zinc formate and acetate, and of lead acetate, the increase of dissociation with dilution is greater than for the other salts, so that the curves for these three compounds cut other curves. In the case of the acetates of calcium, strontium, and barium there is an apparent increase of dissociation with increase of concentration from  $N/4$  to  $N/2$ . For copper malate, the ratio is less than unity so that, probably, complex molecules are present. The concentrations of the copper ions in solutions of copper malate, citrate, glycerate, and salicylate were also calculated by the determination of the E.M.F. of copper chains containing these salts; the existence of complex molecules was indicated in the case of the three first salts, but not in the case of the salicylate, results in accord with the cryoscopic observations (Kahlenberg, Abstr., 1896, ii, 6). Magnesium fumarate was found to be more highly dissociated than magnesium maleate, a result which is in accord with Ostwald's law concerning the dissociation of dibasic acids (Abstr., 1892, 1145). L. M. J.

**Molecular Weights of Liquids.** By CLARENCE L. SPEYERS (*J. Physical Chem.*, 1898, 2, 347—361 and 362—363).—The author applies the equation  $n_1/(n_2 + n_1) = (p - p')/p$ , in which  $n_1$  is the number of molecules of one constituent of a homogeneous mixture,  $n_2$ , the number of molecules of the other constituent,  $p$ , the vapour pressure in the pure state of that constituent to which  $n_2$  refers, and  $p'$ , the

vapour pressure of the same constituent after the other constituent has been mixed with it, to the experimental results obtained by Linebarger and Raoult. He concludes that where discrepancies arise, these can be accounted for by association or dissociation of the constituents as given by the fundamental equation. He also shows that when two liquids are not miscible in all proportions, the separation of a second phase shows the sudden formation of more complex molecules on the part of one constituent.

H. C.

**Velocity of Hydrolysis of Maltose.** By ALEXIUS VON SIGMOND (*Zeit. physikal. Chem.*, 1898, 27, 385—400).—The velocity of hydrolysis of maltose was determined, hydrochloric acid being employed as the hydrolytic agent; the reaction was found to be of the first order, as in the case of sugar inversion, but the velocity increases slightly with the maltose concentration. The effect of rise of temperature was examined, and it was found that the exponential formula of Arrhenius (*Abstr.*, 1889, 1103) applies here also, but the constant  $A$  of the formula being greater for maltose than for cane-sugar, the temperature effect is more marked in this case. The catalytic effects of hydrochloric, sulphuric, and oxalic acids were found to be in the ratio 100:40.5:14.1, whilst for cane-sugar the values are 100:53.7:18.2, so that, although the order is the same, yet the velocity is dependent, not only on the acid, but also on the sugar employed. The velocity-constants for the hydrolysis of cane-sugar and maltose by acetic acid were compared at 69.24°, the ratio being found to be 1133, but, owing to the different effects of temperature, this ratio would not remain constant for different temperatures.

L. M. J.

**Catalytic Action of Platinum Black.** By ALEXANDER DE HEMPTINNE (*Zeit. physikal. Chem.*, 1898, 27, 429—441).—Mond, Ramsay, and Shields (*Abstr.*, 1898, ii, 599) have shown that the formation of a compound of platinum and hydrogen during the occlusion of the gas is very doubtful, and the author hoped to solve the question by the examination of the phenomena of occlusion at very low temperatures, since it seems probable that, if due to the formation of a compound, the occlusion would then be greatly diminished. The absorption of hydrogen by carbon, which appears to be purely mechanical, was found to be far greater at -78° than at +15°, but in the case of platinum the reverse obtained, the absorption in all the experiments being greater at the higher temperature, whilst, if the absorption tube is allowed to slowly regain the higher temperature, a marked absorption of the gas occurs at about -40°. Freshly prepared platinum black possesses a very great absorptive power, even at the temperature of liquid air, so that at -190° it induces the combination of oxygen and hydrogen. The absorption of carbonic oxide is completely analogous to that of hydrogen, and, according to Harbeck and Lunge, a definite compound of platinum and the gas exists (*Abstr.*, 1898, ii, 166). For palladium and hydrogen, different results were obtained, the absorption being greater at the low temperature, although with carbonic oxide the results are similar to those obtained in the case of platinum. It was

here noticed, also, that palladium which has been in equilibrium with carbonic oxide is in some respects altered, and has lost its power of absorbing hydrogen until a temperature of about  $-20^{\circ}$  is reached, when a sudden, great absorption occurs. The explanation of the phenomena must be deferred, but in the case of platinum and hydrogen, the formation of a compound appears to be indicated. L. M. J.

**Catalytic Action in the Oxidation of Iodide by Bromic Acid.** By NIKOLAI SCHILOFF (*Zeit. physikal. Chem.*, 1898, 27, 513—518).—Catalytic actions in the above reaction were investigated for a large number of acids, salts, and organic compounds; acids usually cause acceleration, salts either acceleration or retardation, whilst neutral organic compounds have no effect. The greatest accelerative effects were those of potassium chromate and dichromate, ferrous and ferric salts, and pyrogallol, whilst sodium phosphite and sulphite, nitrobenzene, and resorcinol produced the greatest retardation. If the acceleration be measured by the expression  $1/t_x - 1/t_0$ , where  $t_x$  and  $t_0$  are the times required for the same amount of oxidation in the presence and absence respectively of the catalytic agent, it is found that in the case of potassium molybdate and chromate, the acceleration is a linear function of the concentration for very low concentrations only.

L. M. J.

**Reaction between Potassium Persulphate and Potassium Iodide; Catalysis in the same Reaction.** By THOMAS S. PRICE (*Zeit. physikal. Chem.*, 1898, 27, 474—512).—The reaction may be represented thus:  $S_2O_8^{2-} + 2I^- = 2SO_4^{2-} + I_2$ , and hence appears to be of the third order. The velocity constants as calculated for reactions of both second and third order were obtained; those for the second order are slightly more constant, but the results obtained thus are untrustworthy. The order may, however, be calculated by the expression  $n = \log(dc_1/d\theta_1 \cdot dc_2/d\theta_2) / \log c_1/c_2$ , where  $dc/d\theta$  is the rate of change of concentration at the concentration  $c$ ; the value  $n = 2.4$  is so obtained, again an uncertain result. If the time necessary for any given fractional change be found for any initial concentration  $A$ , then in a reaction of the first order  $t = \text{constant}$ , for the second order  $At = \text{constant}$ , &c. The values of  $t$ ,  $At$ , and  $A^2t$  are, therefore, compared for a fractional change of one-fourth, and it is seen that the values  $At$  increase and those of  $A^2t$  decrease with dilution, so that definite results are not obtained. If the reaction is of the second order, however, equivalent changes in the concentration of both compounds should produce equal effects, and this being found to be the case, the author considers the reaction to be of the second order. This result may indicate the molecular formula  $KSO_4$ , which is not in accord with former work (*Abstr.*, 1893, ii, 572), or that the order of the reaction depends, not on the number of molecules, but of compounds reacting. The author does not, however, discuss either these or any other possible explanations. Various salts were found to have a catalytic effect on the reaction, that of dissociated iron and copper salts being very marked. In the case of ferrous and copper sulphates, the acceleration (measured by the quantity  $1/t_n - 1/t_0$ ) was found to be proportional to the concentration. Salts of nickel and cobalt cause a slight acceleration, but chromic acid,

potassium dichromate, manganese sulphate, sodium nitrite, zinc sulphate, magnesium sulphate, and potassium sulphate were inactive. Mixtures of ferrous and copper sulphates were found to cause an acceleration almost double of that calculated additively, so that the catalytic effect of each is increased by the presence of the other. Inactive compounds, such as zinc sulphate, have no effect on the catalysis caused by copper sulphate, but decrease the influence of ferrous sulphate. The addition of acid, at first causes a decrease in the catalytic effect of copper sulphate, but a constant value is soon reached.

L. M. J.

**Atomic Weight of Tellurium in Relation to the Multiple Proportions of the Atomic Weights of other Simple Substances.** By HENRY WILDE (*Compt. rend.*, 1898, 127, 613—616).—This paper is largely controversial, and does not lend itself to abstraction.

W. A. D.

**Position of Tellurium and Iodine in the Periodic System.** By HENRY WILDE (*Compt. rend.*, 1898, 127, 616—618).—Metzner (*Abstr.*, 1898, ii, 572) has recently obtained results which indicate that the atomic weight of tellurium (128) is greater than that of iodine; this, it is maintained, necessitates a change in position of these elements in the periodic system, and involves a contradiction of the accuracy of the latter. It is contended that if the order of the atomic weights of the elements is exactly followed, the law of periodicity of their properties ceases to be valid; also, that Mendeléeff's success in predicting the existence of gallium, scandium, and germanium was simply a consequence of Dumas' classification of the elements in families and to the relations shown to exist between the "equivalents" of the elements of a family. Boron, judging from its properties, should belong to the group containing phosphorus and vanadium (compare Étard, *Abstr.*, 1881, 20), and should not be considered as the analogue of aluminium and gallium, as required by Mendeléeff's classification, whilst the position of gold, mercury, and lead is also looked on as abnormal.

W. A. D.

**Laboratory Sodium Burner.** By CARL PULFRICH (*Chem. Centr.*, 1898, i, 763; from *Zeit. Instrumentk.*, 18, No. 2).—In this apparatus, a round sheet of asbestos is held horizontally above a Bunsen burner by means of a clamp, which slides on a vertical rod attached to the burner. The sheet can be rotated so that the flame of the burner passes through one of several round holes, about 1 cm. wide, which are cut near the periphery of the sheet. By heaping the illuminating salt, preferably sodium nitrate, on account of its low melting point, or sodium bromide, which gives a more brilliant light, round the hole, a luminous flame may be maintained for a long time. The shape of the flame may be altered by changing the form of the hole. The apparatus, fitted also with a detachable carrier for platinum wires, is made by C. Desaga, in Heidelberg.

E. W. W.

## Inorganic Chemistry.

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**Presence of Free Hydrogen in the Atmosphere.** By ARMAND GAUTIER (*Compt. rend.*, 1898, 127, 693—694).—The air in the neighbourhood of towns contains variable quantities of combustible carbon compounds, only minute traces of which can be detected in the atmosphere of mountainous regions, and in sea air. On the other hand, pure air contains a small amount of free hydrogen, the proportion varying from 11 to 18 c.c. per 100 litres. G. T. M.

**Decomposition of Hydrogen Peroxide by Silver Oxide.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1897, [vii] 11, 217—222).—An indefinite amount of hydrogen peroxide may be decomposed by a small quantity of silver oxide, the whole of the oxygen evolved being furnished by the peroxide, whilst the silver oxide is itself changed into the sesquioxide,  $\text{Ag}_2\text{O}_3$ , and free silver. If, however, the silver oxide is in excess, or if the solutions employed are not sufficiently dilute, or if excess of free alkali is present, then some oxygen is given up by the silver sesquioxide.

In employing this reaction for the estimation of hydrogen peroxide, it is preferable to employ dilute solutions, to prepare the silver oxide beforehand, and to avoid excess of this reagent; if the oxide be formed in the presence of the hydrogen peroxide by the action of caustic potash on silver nitrate, the heat evolved in this reaction promotes the decomposition of silver sesquioxide, which then gives off oxygen.

G. T. M.

**Decomposition of Hydrogen Peroxide by Ammoniacal Silver Oxide.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1897, [vii], 11, 223—230. Compare preceding abstract).—When hydrogen peroxide is added to a suspension of ammoniacal silver oxide in water, a portion of the latter is reduced to metallic silver, and in so doing evolves oxygen; with excess of peroxide, the reduction is almost complete. When a solution of ammoniacal silver nitrate is added to hydrogen peroxide, the latter is decomposed, but only a slight reduction of silver oxide takes place; when the peroxide is added to the ammoniacal silver nitrate, four-fifths of the silver is precipitated in a crystalline form. When a solution of silver nitrate and hydrogen peroxide is added to ammonia, or *vice versa*, more or less silver is always precipitated, the amount depending on the order of mixing and the strength of the solutions. No appreciable quantity of silver sesquioxide appears to be formed when ammoniacal solutions are employed (compare previous abstract). Ammoniacal silver nitrate (1 mol.) rapidly decomposes excess of hydrogen peroxide (30 mols.), but with a smaller proportion the reaction is slow and incomplete. Alkaline solutions of potassium silver cyanide and sodium silver thiosulphate have no action on hydrogen peroxide; ammoniacal silver

chloride causes a slow evolution of oxygen, which becomes more rapid when caustic potash is added, crystalline silver being deposited.  
G. T. M.

**Solubility of Iodine and Bromine in Water.** By F. DIETZE (*Chem. Centr.*, 1898, i, 1094; from *Pharm. Zeit.*, 43, 290).—According to the author, when iodine is shaken with water at 15°, 1 part dissolves in 3750 parts of water, whilst by heating water and iodine together and then cooling to 15°, 1 part of iodine is obtained in solution in 3500 parts of water. The solubility of iodine increases with the temperature, and at 30° 1 part dissolves in 2200 parts of water. The German pharmacopœia gives the solubility of iodine in water as 1 part in 5000, and that of bromine as 1 part in 30 parts of water. The latter, according to the author, is correct. E. W. W.

**Preparation of Hydrogen Chloride, Bromide, and Iodide for Laboratory Purposes.** By AD. VANDENBERGHE (*Chem. Centr.*, 1898, i, 916—917; from *Maandbl. naturw.*, 22, 35—36).—When concentrated sulphuric acid is added drop by drop to strong hydrochloric acid, the liberated gas usually contains free chlorine and ferric chloride which are derived from impurities in the hydrochloric acid; according to the author, the gas may be purified by adding ferrous sulphate to the hydrochloric acid, whereby the chlorine is retained and the ferric chloride reduced to ferrous chloride. In order to test for free chlorine by means of starch paper, a solution of the gas must be used, as gaseous hydrogen chloride with starch paper always produces a blue coloration owing to oxidation of the acid.

Pure hydrogen bromide and hydrogen iodide may be obtained in a constant stream by allowing a solution of the acid, prepared by means of phosphorus, to drop on to phosphoric anhydride. In the case of hydrogen iodide, the first portions of the gas contain free iodine, which can be removed by passing it through a solution of calcium iodide. The gases are dried by means of phosphoric anhydride. When prepared from organic substances, the gases always contain volatile organic compounds.  
E. W. W.

**Density and Molecular Weight of Ozone.** By WILHELM STAEDEL (*Ber.*, 1898, 31, 3143—3144).—The author points out that the assumption recently made by Ladenburg (this vol., ii, 18, 89) in his attempt to determine the density of ozone, that 1 molecule of iodine is liberated by 1 molecule of ozone is purely empirical, and in reality assumes the very quantity which is to be determined. The molecule of ozone may be expressed by the formula  $O_2 + nO$ , so that each molecule of ozone liberates  $n$  molecules of iodine. Without independent information as to the value of  $n$ , it is impossible to deduce the density of ozone from the density of a mixture of this gas with oxygen, and an estimation of the amount of iodine liberated per unit volume of this mixture.  
A. H.

**Density and Molecular Weight of Ozone.** By MAX GRÖGER (*Ber.*, 1899, 31, 3174—3176).—In a recent paper by Ladenburg (this vol., ii, 18, 89) the density of a specimen of ozonised oxygen is given, and also the weight of iodine liberated by the gas when in



contact with potassium iodide, and by means of these numbers, taken in conjunction with the fact that the gas undergoes no alteration in volume during the action referred to, an attempt is made to prove that the molecule of ozone is triatomic. The argument employed is fallacious, as the excess of the density of the ozonised gas over that of pure oxygen represents the weight of oxygen available for the liberation of the iodine, and the amount of the latter set free may be at once calculated if that excess be known, whatever be the molecular weight of the ozone concerned. A. L.

**Hydrates of Gases.** By P. VILLARD (*Ann. Chim. Phys.*, 1897, [vii], 11, 289—394).—The author gives full details of the apparatus employed by him in obtaining the hydrates of the following gases, nitrous oxide, carbonic anhydride, acetylene, ethylene, methylic chloride, and sulphurous anhydride, and in investigating their physical properties (compare *Abstr.*, 1888, 1020, 1241; 1890, 1386; 1895, i, 635; ii, 44, 497).

The preparation of the hydrates of the following liquids, methylic iodide, ethylic chloride, bromide and iodide, methylenic chloride, chloroform, carbon tetrachloride, ethylidenic chloride, chlorethylene ethylenic chloride, and carbon bisulphide is described, and their properties are compared with those of the hydrates of the gases.

The influence of inert gases under pressure on the dissociation of these hydrates is fully discussed. G. T. M.

**Action of Sodammonium on Arsenic.** By C. HUGOT (*Compt. rend.*, 1898, 127, 553—555).—Whereas different products are obtained by the action of sodammonium on phosphorus in presence of liquefied ammonia, according as the phosphorus is present in small quantity only or in excess (*Abstr.*, 1896, ii, 20, and 1898, ii, 573), arsenic gives rise to only one *derivative*,  $\text{AsNa}_3\text{NH}_3$ , under all conditions. In the experiments described, both the arsenic and sodium were carefully purified by distillation, and were allowed to interact under the same conditions as were employed formerly in the case of phosphorus (*loc. cit.*). A brick-red product was obtained, which contained traces of sodamide, and dissolved only sparingly in liquid ammonia; from the latter solution, small crystals of the compound were obtained. W. A. D.

**Compounds of Carbonic Anhydride with Water, Ethylic Ether, and Alcohols.** By WALTHER HEMPEL and JOHANNES SEIDEL (*Ber.*, 1898, 31, 2997—3001).—A weighed quantity of water was sealed in a tube with solid carbonic anhydride; at the ordinary temperature, the liquid formed two layers, the water underneath; on cooling the tube slowly, crystals formed; these began to melt at about  $8^\circ$ . The tube was then cooled to  $-79^\circ$ , opened, furnished with a delivery tube dipping under mercury, and then allowed to rise in temperature; carbonic anhydride was evolved furiously at first, but ceased to come off at  $-25^\circ$ ; at  $-2^\circ$ , the evolution of gas again commenced, and the volume that came off between this temperature and  $+20^\circ$  corresponded with a composition of  $\text{CO}_2 + 8\text{H}_2\text{O}$  for the crystals; another experiment gave results corresponding with  $\text{CO}_2 + 9\text{H}_2\text{O}$ .

Aqueous ether was saturated with solid carbonic anhydride, and the solid that formed was collected on a cooled filter; the loss of weight which it underwent up to  $0^{\circ}$  was taken as carbonic anhydride, and that at  $0-37^{\circ}$  as ether, the rest being water; the error of such an estimation is 2—3 per cent. It was found that the composition of the solid varied with the temperature at which it had been collected. At a very low temperature, little else but carbonic anhydride was present; the amount of ether, and still more that of the water, increased with the temperature of isolation; at  $-50^{\circ}$  the composition corresponded approximately to  $\text{CO}_2 + 4\text{H}_2\text{O} + \text{Et}_2\text{O}$ .

With aqueous ethylic alcohol, a compound  $17\text{CO}_2 + 3\text{EtOH} + \text{H}_2\text{O}$  was obtained. Monocarbonates of alkyl radicles,  $\text{ROH} + \text{CO}_2$ , were obtained by weighing a quantity of the alcohol into a tube, distilling into it excess of liquid carbonic anhydride, and then allowing the excess to evaporate and cooling the tube. The *methyl*, *ethyl*, *tertiary butyl*, and *amyl* compounds melt at  $-57$  to  $-60^{\circ}$ ,  $-61$  to  $-57^{\circ}$ ,  $-15$  to  $-10^{\circ}$ , and  $-60^{\circ}$ ; the mixture with *propylic* alcohol separates, on cooling, into two layers which melt at  $-56^{\circ}$  and  $-50^{\circ}$  respectively. C. F. B.

**Examination of Sodium Phosphate for Sodium Carbonate, and Reaction of Sodium Phosphate with Phenolphthalein.** By BRUNNER [Wetzlar] (*Zeit. anal. Chem.*, 1898, 37, 740—741).—The author cannot confirm Geissler's statement (Abstr., 1898, 458) that pure disodium hydrogen phosphate does not give a pink colour with phenolphthalein. The purest salt obtainable, recrystallised from a solution, which, after being strongly acidified with phosphoric acid, has been boiled for a long time to ensure the complete decomposition of carbonate, exhibits an alkaline reaction with both litmus and phenolphthalein even when its immediate mother liquor is feebly acid. M. J. S.

**Preparation of Lithium and Calcium Ammonias and Corresponding Amides.** By HENRI MOISSAN (*Compt. rend.*, 1898, 127, 685—693).—Dry ammonia gas combines with potassium, sodium, lithium, and calcium, and the superior limit of temperature at which this reaction occurs is  $-20^{\circ}$  for sodium,  $-2^{\circ}$  for potassium,  $20^{\circ}$  for calcium, and  $70^{\circ}$  for lithium; solid ammonia at  $-80^{\circ}$  is without action on these metals. The sodium and potassium ammonias decompose at  $-20^{\circ}$  and  $-2^{\circ}$  respectively, whereas the calcium and lithium compounds are stable at ordinary temperatures.

*Lithium ammonia*,  $\text{Li.NH}_3$ , is obtained as a brownish-red solid when the liquid produced by the action of dry ammonia gas on lithium at ordinary temperatures is rapidly heated to  $70^{\circ}$ ; if produced at lower temperatures, it always contains more ammonia than that demanded by the above formula. When allowed to remain for any length of time at the ordinary temperature, a solution of lithium ammonia in liquid ammonia yields lustrous, transparent crystals of lithamide. This reaction proceeds more rapidly at  $65-80^{\circ}$ , and appears to be independent of the pressure. If solid lithium ammonia heated at  $50^{\circ}$  or  $60^{\circ}$  is exposed to the rapid action of the vacuum pump, ammonia is evolved and crystalline lithium is obtained; if the exhaustion is effected more

slowly at ordinary temperatures hydrogen is also evolved, and the residue consists of lithium and lithamide.

*Calcium ammonia*,  $\text{Ca}, 4\text{NH}_3$ , is obtained as a brownish-yellow solid with a bronzy reflex when crystallised calcium is treated with dry ammonia at  $15^\circ$ — $20^\circ$ ; it evolves ammonia and hydrogen at ordinary temperatures, and is slowly converted into *calcamide*,  $\text{Ca}(\text{NH}_2)_2$ .

Both the lithium and calcium compounds take fire when exposed to air, and are far less soluble in liquid ammonia than the corresponding sodium compound. These substances are being investigated both by the author and by Güntz, the latter having independently examined the action of ammonia on calcium obtained from lime by reduction with magnesium.

G. T. M.

**Properties of Calcium.** By HENRI MOISSAN (*Compt. rend.*, 1898, 127, 584—590).—Pure calcium, prepared by the author's method (*Abstr.*, 1898, ii, 578), separates from fused sodium in hexagonal crystals, which have a sp. gr. = 1.85, and melt, in a vacuum, at  $760^\circ$ ; after solidifying, the metal is less malleable than sodium or potassium, and is somewhat brittle, showing a crystalline fracture. When free from nitride, its surface is brilliant, and silver white in colour. When exposed at a dull, red heat to a stream of hydrogen, the crystalline hydride,  $\text{CaH}_2$ , is formed. Contrary to Matthiessen's statement (*Annalen*, 1855, 93, 277), calcium is not acted on by chlorine at the ordinary temperature, but at  $400^\circ$  vigorous action occurs, calcium chloride being formed; chlorine, however, readily combines at the ordinary temperature with calcium containing nitride, a fact which explains Matthiessen's result. The metal is not acted on by bromine or iodine at the ordinary temperature, but burns vigorously when heated in the vapours of these elements. It ignites in oxygen at  $300^\circ$ , and burns brilliantly, the oxide formed being partially fused and volatilised. When calcium is gently warmed in air, it burns with brilliant scintillations; at a dull red heat, a partially fused mass is obtained, which is decomposed by water, giving ammonia and calcium hydroxide; no peroxide appears to be formed. At  $400^\circ$ , calcium and sulphur combine with incandescence, the sulphide obtained being a white powder, which dissolves in dilute hydrochloric acid without depositing sulphur. With selenium and tellurium, calcium also combines, whilst it burns with incandescence in the vapour of phosphorus, giving a product which decomposes water to form spontaneously inflammable hydrogen phosphide. Arsenic, at the temperature at which it sublimes, gives, with calcium, a dark-coloured, fused mass, which decomposes water, forming hydrogen arsenide and a black, insoluble powder; *calcium antimonide*, however, prepared similarly, does not yield hydrogen antimonide when decomposed by water or dilute hydrochloric acid, but only a black, insoluble powder, and the same is true of the *compounds* of calcium and bismuth, although here hydrogen is also evolved. At a red heat, calcium combines vigorously with lamp-black, yielding only one carbide,  $\text{CaC}_2$ , whatever proportions are employed; *calcium silicide*, prepared by strongly heating a mixture of its constituent elements, is not decomposed by water, but dissolves in hydrochloric

acid, slowly at the ordinary temperature, rapidly when heated, giving hydrogen, silicon hydride, and a large quantity of silicon.

Calcium does not readily dissolve in potassium, but yields somewhat brittle *alloys* with magnesium, zinc, and nickel; with tin, a crystalline *alloy* is obtained, which contains 3.82 per cent. of calcium, has a sp. gr. = 6.70, and decomposes water very slowly. With mercury, calcium combines at the ordinary temperature to form a crystalline *amalgam*, heat being evolved; although no calcium hydride is formed when this is distilled in an atmosphere of hydrogen at 400°, the amalgam is rapidly decomposed by nitrogen, under similar conditions, giving calcium nitride, and blackens when exposed to air at the ordinary temperature, owing to the fixation of both oxygen and nitrogen.

At a red heat, calcium liberates the alkali metal from potassium or sodium chloride; the corresponding iodides are, however, not affected. When calcium is fused with calcium iodide, a *subiodide* appears to be formed, which is also obtained in the form of red, transparent crystals, when calcium iodide is decomposed electrolytically; calcium chloride, under the like conditions, behaves in a similar manner.

Calcium is only slowly acted on by pure water at the ordinary temperature, hydrogen being evolved; when heated in sulphurous anhydride, it becomes incandescent, a complex change taking place. In nitric oxide, it burns brilliantly, giving rise to calcium oxide only, no nitride being formed. At a red heat, calcium combines with phosphoric anhydride with explosive violence; at 600°, it reduces boric anhydride to boron, without the production of calcium boride (Moissan and Williams, *Abstr.*, 1898, ii, 116), and at a red heat decomposes silica, giving calcium silicide and a small quantity of silicon. When slowly heated in carbonic anhydride, it is only partially acted on, carbon, calcium oxide, and a small quantity of calcium carbide being formed; when, however, the heating is rapid, the whole of the metal is converted into oxide and carbide. With carbonic oxide, the action is always incomplete, some carbon being liberated. Uranium sesquioxide, and titan and vanadic acids are reduced, when heated with calcium, to lower oxides.

Fuming nitric acid acts only very slowly on pure calcium; when very slightly diluted, however, the action is rapid. Cold fuming sulphuric acid is immediately reduced by the metal, sulphur and sulphurous anhydride being formed, whilst sulphuric monhydrate gives rise, in addition, to hydrogen sulphide. Both hydrochloric and acetic acids dissolve calcium with evolution of hydrogen. When heated in gaseous hydrogen chloride, the metal becomes incandescent and is converted into chloride; hydrogen sulphide, under similar conditions, produces calcium sulphide.

Calcium is not acted on by ammonia gas in the cold, but at a dull, red heat it is converted into a mixture of hydride and nitride; with liquefied ammonia at - 40°, calcium gives rise to *calcium ammonia*, a reddish-brown solid, the study of which is being continued. Calcium decomposes boron bromide at a dull red heat, giving calcium boride and boron; the latter is also obtained on heating a mixture of calcium and boron nitride, calcium nitride being formed. At a dull

red heat, calcium is only partially acted on by acetylene, ethylene, and methane, a crust of carbon, carbide, and nitride being formed, which prevents further action.

W. A. D.

**Calcium Amalgam.** By JULES FEREÉ (*Compt. rend.*, 1898, 127, 618—620).—When a well cooled 50 per cent. aqueous solution of calcium chloride is decomposed electrolytically, using a mercury electrode and a porous diaphragm, so arranged that the chlorine generated cannot act on the calcium amalgam formed, the latter is found to be much richer in calcium than the amalgam obtained by Maquenne (*Bull. Soc. Chim.*, 1892, 366); when submitted to distillation in a vacuum, 1·2 per cent. of a compound,  $\text{Ca}_3\text{Hg}_4$ , is left. The amalgam is a porous, whitish-green substance, which rapidly oxidises in air, and readily decomposes water. When heated in an atmosphere of hydrogen, it loses mercury, but does not form calcium hydride. Its remaining properties are identical with those given by Moissan (preceding abstract). In conclusion, the author confirms the formula  $\text{Ca}_3\text{N}_2$  for calcium nitride, by analyses based on its conversion by dilute sulphuric acid into calcium and ammonium sulphates.

W. A. D.

**Preparation and Properties of Calcium Nitride.** By HENRI MOISSAN (*Compt. rend.*, 1898, 127, 497—501).—Calcium at a dull red heat combines with nitrogen with incandescence to form a nitride,  $\text{Ca}_3\text{N}_2$ . The calcium is best placed in nickel dishes in a nickel tube. The nitride forms transparent, brownish-yellow, microscopic crystals, which are deeper in colour if they contain unaltered calcium; sp. gr. = 2·63 at 17°. It is attacked by hydrogen below dull redness, with formation of the hydride and ammonia; by chlorine and bromine, with incandescence in the cold, or on very gently heating, and by iodine at dull redness; by oxygen, below a red heat, with incandescence; by sulphur, at about 500°, and by phosphorus vapour at a cherry-red heat, but not by boron or silicon at 1000°. Carbon has no action on the nitride at 800°, but completely decomposes it in a few minutes in the electric furnace; at 1200°, small quantities of cyanide are formed.

Sodium, potassium, and magnesium have no action on the nitride at a red heat; nitric oxide attacks it slowly below dull redness and violently, with incandescence, at a higher temperature. Dilute acids dissolve the nitride, but no action takes place in complete absence of water. Alcohol gradually decomposes it at the ordinary temperature, with production of ammonia and calcium ethoxide; ethylic chloride attacks it at a dull red heat, with production of methane, ammonium chloride, and calcium chloride.

When calcium can be prepared on a large scale, it can readily be made to combine with nitrogen separated from the air, and the nitrogen can be converted into ammonia by the action of steam on the nitride.

C. H. B.

**Action of Water on Calcium Carbide.** By ERNEST CHUARD (*Bull. Soc. Chim.*, 1897, [iii], 17, 678—679).—The gas evolved when water acts on calcium carbide contains 0·03—0·06 per cent. of

ammonia, produced by the action of water on the calcium nitride, which is always present. Ammonia is also found in the residues, and is derived from the action of water on calcium cyanate.

The presence of hydrogen sulphide and phosphine in the acetylene has also been proved. The latter impurity forms 0.018—0.032 per cent. of the gas, and its presence accounts for the insecticidal properties of acetylene prepared in this manner. By introducing calcium phosphate into the material used in preparing the calcium carbide, the relative amount of phosphine in the gas, and therefore the insecticidal power, is greatly augmented, and it is hoped that it may find an application in the treatment of phylloxera-infested vines.

A. L.

**Simple and Complex Magnesium Pyrophosphates.** By MARCELLIN P. BERTHELOT and GUSTAVE ANDRE (*Ann. Chim. Phys.*, 1897, [vii], 11, 190—197).—The precipitate obtained, either from sodium pyrophosphate in the estimation of pyrophosphoric acid (Abstr., 1897, ii, 140), or from sodium metaphosphate under similar conditions, consists of the double salt  $\text{Mg}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 + n\text{H}_2\text{O}$  mixed with  $\text{Mg}_3\text{Na}_2(\text{P}_2\text{O}_7)_2$  in the proportion of three of the former to one of the latter; it also contains a small quantity of an alkali acetate. The double salt retains the whole of its ammonia, even when heated to  $110^\circ$ , or when repeatedly washed with dilute acetic acid; the latter treatment removes some of the magnesium, but the quantity of phosphoric acid thereby rendered soluble is inconsiderable, and only amounts to 0.1 per cent.

Excess of ammonium salts is necessary to ensure the complete precipitation of pyrophosphoric acid. A boiling solution of sodium pyrophosphate, treated with a mixture of magnesium chloride and acetic acid, yields a precipitate of the simple pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ ; but the filtrate still contains nearly one-third of the total phosphorus.

G. T. M.

**Artificial Boracites containing Iodine.** By H. ALLAIRE (*Compt. rend.*, 1898, 127, 555—557).—The author describes several substances containing iodine, which are analogous with natural boracite in composition and crystalline habit. The *magnesium-boracite*,  $6\text{MgO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{MgI}_2$ , is obtained only with difficulty by passing the vapour of magnesium iodide over heated magnesium borate; it is also formed, but in an impure state, by the action of iodine on a mixture of magnesium and its borate heated in an atmosphere of hydrogen; it forms colourless cubes and tetrahedra. The *zinc boracite*,  $6\text{ZnO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{ZnI}_2$ , is, however, readily prepared by passing a stream of carbonic anhydride laden with iodine vapour over a heated mixture of zinc and zinc borate; the *cadmium* compound,  $6\text{CdO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{CdI}_2$ , and the *manganese* and *iron* compounds of corresponding composition, are prepared similarly, and closely resemble the zinc derivative, but the *nickel* compound,  $6\text{NiO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{NiI}_2$ , is yellow, and the *cobalt* compound,  $6\text{CoO} \cdot 8\text{B}_2\text{O}_3 \cdot \text{CoI}_2$ , violet in colour.

A better method of preparing boracites containing chlorine than has been hitherto given (compare Rousseau and Allaire, Abstr., 1893, ii, 468, and 1894, ii, 413) consists in passing hydrogen chloride

over the corresponding amorphous borate at a dull red heat; the product is well crystallised and pure. Several of the artificial boracites which contain iodine can be prepared by fusing molecular proportions of the iodides of sodium and of the metal chosen with boric acid and a small quantity of borax, in a steel crucible on to which is fitted a cover furnished with a small iron exit-tube; this is necessary in order to prevent aqueous vapour from the furnace coming into contact with the contents of the crucible. W. A. D.

**Crystallised Basic Cupric Chlorate.** By LEON BOURGEOIS (*Bull. Soc. franç. Min.*, 1898, 21, 170—176).—Crystals of cupric chlorate,  $\text{Cu}(\text{ClO}_3)_2 + 6\text{H}_2\text{O}$ , fuse at  $65^\circ$  in their water of crystallisation to a blue, syrupy liquid; decomposition commences at  $100^\circ$ , and takes place rapidly at  $110$ — $140^\circ$  with evolution of gas and formation of the basic salt  $\text{Cu}(\text{ClO}_3)_2 \cdot \text{Cu}(\text{OH})_2$ . Bluish-green crystals, 1—2 mm. across, of this basic salt are obtained when the heating is effected in a flask on a sand-bath. Smaller crystals are obtained by heating a solution of cupric chlorate with fragments of marble or with carbamide in a sealed tube at  $130^\circ$ . The crystals have a sp. gr. = 3.55; they are monosymmetric, and are isomorphous with the corresponding nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot \text{Cu}(\text{OH})_2$ . When cupric nitrate is heated in the same manner, orthorhombic crystals of the mineral gerhardtite, a dimorphous form of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{Cu}(\text{OH})_2$ , are formed. Cupric bromate yields a greenish blue, crystalline powder of basic bromate. L. J. S.

**New Hydrate of the Saline Oxide of Chromium [ $\text{Cr}_3\text{O}_4$ ]**  
By GEORGES BAUGE (*Compt. rend.*, 1898, 127, 551—553).—When chromous sodium carbonate (Abstr., 1898, ii, 294), or, better, the corresponding potassium compound (*ibid.*, 598), is boiled with water in an atmosphere of carbonic anhydride, a somewhat unstable, brick-red powder is precipitated, having apparently the composition  $\text{Cr}_3\text{O}_4 + 4\text{H}_2\text{O}$ ; when dried in a vacuum at  $100^\circ$ , it gives rise to a yellowish brown compound,  $\text{Cr}_3\text{O}_4 + 3\text{H}_2\text{O}$ , which has a sp. gr. = 3.49, and is converted into chromium sesquioxide by the action at  $250^\circ$  of water-vapour, hydrogen chloride, or an inert gas, hydrogen being evolved; it is also decomposed by chlorine at a dull red heat, giving chromyl chloride, water, and hydrogen chloride. Although stable in dry air at the ordinary temperature, it is rapidly oxidised to chromium sesquioxide in presence of water or when heated; by hydrogen sulphide, it is converted at a somewhat elevated temperature into a crystalline sulphide, whilst it rapidly reduces dilute sulphuric acid at  $40^\circ$ , hydrogen sulphide being evolved if a large quantity of the oxide is employed. When the latter is dissolved in concentrated hydrochloric acid, a mixture of chromous and chromic chlorides is obtained. All attempts to convert the oxide  $\text{Cr}_3\text{O}_4 + 3\text{H}_2\text{O}$  into the compound  $\text{Cr}_3\text{O}_4 + \text{H}_2\text{O}$  described by Peligot (*Ann. Chim. phys.*, [iii], 1844, 12, 539) failed. W. A. D.

**Iron Chromium Carbide and Iron Molybdenum Carbide.** By PEREY WILLIAMS (*Compt. rend.*, 1898, 127, 483—484).—*Iron chromium carbide*,  $3\text{Fe}_3\text{C} \cdot 2\text{Cr}_3\text{C}_2$ , intermediate between the carbides  $3\text{Fe}_3\text{C} \cdot \text{Cr}_3\text{C}_2$  and  $\text{Fe}_3\text{C} \cdot 3\text{Cr}_3\text{C}_2$  described by Carnot and Goutal, is obtained by heating a mixture of chromic oxide, 200 grams; iron, 200 grams; and petroleum

coke, 70 grams, in a carbon crucible for 5 minutes with an arc from a current of 45 volts and 900 ampères. The crystalline ingot thus obtained, which resembles ferrochrome in appearance, is treated with aqua regia at 100°, and any graphite that remains is removed by levigation with bromoform. The carbide forms very brittle needles with a metallic lustre and the colour of nickel; sp. gr. = 7.22 at 19°; hardness between glass and rock crystal. It is attacked by chlorine at a red heat, and also, although more slowly, by bromine and iodine; by oxygen and water vapour at about 500°, and by gaseous or dissolved hydracids, but not by nitric acid or aqua regia.

*Iron molybdenum carbide*,  $\text{Fe}_3\text{C}, \text{Mo}_2\text{C}$ , is prepared in an exactly similar way from a mixture of molybdenum dioxide (prepared by heating ammonium molybdate), 130 grams; iron, 300 grams; and petroleum coke, 50 grams. The ingot is treated with hydrochloric acid instead of aqua regia, and the insoluble residue is separated into two parts by means of a magnet. The non-magnetic part consists of graphite, which is separated by means of bromoform or methylenic iodide, and the iron molybdenum carbide, which consists of a grey powder of microscopic, arborescent crystals resembling those of antimony; sp. gr. = 7.47 at 18°. The carbide is attacked by chlorine, bromine, iodine, or the gaseous or dissolved hydracids when heated, but is most readily dissolved by dilute nitric acid.

In the preparation of these and similar carbides there is always a relation between the proportions of carbide and of graphite respectively in the ingot obtained; the one seems to vary inversely as the other, and the manner of cooling exercises a considerable influence on the proportions.

C. H. B.

**Preparation of Tungsten, Molybdenum, Chromium, and Manganese Silicides.** By HENRY N. WARREN (*Chem. News*, 1898, 78, 318—319).—When aluminium is added to a well fused mixture of 2 parts of cryolite with 1 part of sodium silicate, reaction proceeds tranquilly, which is not the case when potassium silicofluoride is employed. A mass of graphitoidal silicon mixed with aluminium is obtained, from which the latter is removed by means of hydrochloric acid.

*Manganese silicide* is obtained when any oxide of manganese is reduced at a full white heat in presence of excess of silicon; it contains 30 to 40 per cent. of silicon, has a white, metallic lustre, is fusible, brittle, and hard enough to scratch glass.

*Chromium silicide* resembles the manganese compound, but is less fusible, harder, and offers greater resistance to reagents.

*Tungsten and molybdenum silicides* require the full heat of an oxygen-hydrogen furnace for their preparation, and when the reaction is properly conducted, they form well fused masses; they are crystalline and very hard, in some cases scratching quartz, tungsten silicide being the harder. All these silicides are decomposed readily by hydrofluoric acid and by chlorine at a red heat; other acids, however, only act on them with difficulty.

D. A. L.

**Electrolytic Production of Crystalline Tungsten.** By L. A. HALLOPEAU (*Compt. rend.*, 1898, 127, 755—756. Compare Moissan, *Abstr.*, 1896, ii, 606, and this vol., ii, 32).—Lithium paratungstate



heated to  $1000^{\circ}$  is submitted for 3 hours to the action of an electric current of 3 amperes with an E.M.F. of 15 volts. The product, after extraction with hot water, concentrated hydrochloric acid, and lithium hydroxide solution, consists of crystalline tungsten, which is contaminated with more or less platinum derived from the electrodes. The tungsten thus obtained forms opaque prismatic crystals with a metallic lustre, and having an acicular habit like those of silicon.

G. T. M.

**Tungsten Tetriodide.** By ED. DEFACQZ (*Compt. rend.*, 1897, 127, 510—512).—*Tungsten tetriodide*,  $WI_4$ , obtained by the action of an excess of liquid hydrogen iodide on tungsten hexachloride at  $110^{\circ}$ , is a black, crystalline substance of sp. gr. 5.2 at  $18^{\circ}$ , insoluble in water, ether, chloroform, and turpentine, but soluble in absolute alcohol; it does not melt, and does not sublime without decomposing. Hydrogen reduces it below a red heat, chlorine displaces the iodine at the ordinary temperature, and bromine displaces it at  $100^{\circ}$ . Water decomposes it slowly in the cold, and rapidly on boiling, and it is readily attacked by dilute hydrochloric and sulphuric acids, and by nitric acid and aqua regia, which convert it into tungstic acid. Alkali hydroxides and carbonates, whether in solution or fused, and fused potassium hydrogen sulphate also readily decompose the tetriodide (compare Abstr., 1898, ii, 521).

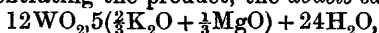
C. H. B.

**Crystallised Tungsten Dioxide and a Tungstolithium Tungstate.** By L. A. HALLOPEAU (*Compt. rend.*, 1898, 127, 512—514).—When lithium paratungstate is heated in a current of hydrogen at about the melting point of glass for 45 minutes, it is completely reduced to tungsten dioxide, which is obtained as an opaque, brown, microcrystalline powder with a coppery lustre, by treating the product of reduction successively with boiling water, concentrated hydrochloric acid, and lithium hydroxide solution (20:100), and finally washing thoroughly with warm water. The dioxide thus prepared is of constant composition; it is not attacked by hydrochloric and sulphuric acids, or by concentrated solutions of the alkalis either at the ordinary temperature or on heating. Nitric acid oxidises it to tungstic acid, and when heated in oxygen it burns and yields pure microcrystalline tungstic anhydride.

If the paratungstate is fused with a fragment of tin for about an hour, and the product is treated in the same way as the product of reduction in hydrogen, it yields a very deep blue powder consisting of microscopic prisms of the "tungsten bronze,"  $Li_2W_5O_{15}$  or  $Li_2O.WO_3 + WO_2.3WO_3$ , analogous to the sodium compound prepared in the same way.

C. H. B.

**Action of Metallic Sulphates on Potassium Paratungstate.** By L. A. HALLOPEAU (*Compt. rend.*, 1898, 127, 620—621. Compare von Knorre, Abstr., 1885, 1184, and 1886, 597).—On mixing solutions of potassium paratungstate and magnesium sulphate in molecular proportion, and concentrating the product, the double salt,



separates in hexagonal prisms; it is almost insoluble in cold water, but dissolves more readily in hot, and loses  $17\text{H}_2\text{O}$  at  $100^\circ$ . When solutions of potassium paratungstate and manganese sulphate are mixed, the salt,  $12\text{WO}_3, 3\text{K}_2\text{O}, 2\text{MnO} + 16\text{H}_2\text{O}$ , is immediately precipitated as a colourless, crystalline powder, which loses  $10\text{H}_2\text{O}$  when dried at  $100^\circ$ . The zinc double salt is crystalline, but cannot be obtained pure, whilst the cadmium and most other double salts are amorphous.

W. A. D.

**Crystallised Uranium Phosphate.** By LEON BOURGEOIS (*Bull. Soc. Philomatique, Paris*, 1897, 9, 125—130; and *Bull. Soc. franç. Min.*, 1898, 21, 32—39).—From a solution of precipitated uranium phosphate in hot water acidified with hydrochloric acid, yellow crystals, 2—3 mm across, of  $\text{H}(\text{UO}_2)\text{PO}_4 + 4\text{H}_2\text{O}$  are deposited after some time. These have the sp. gr. 3.03, and are square, tetragonal plates with angles closely related to those of the minerals cupro-uranite,  $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 + 8\text{H}_2\text{O}$ , and calco-uranite,  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 + 8\text{H}_2\text{O}$ , &c. Crystallised cupro-uranite has often been prepared by the action of copper phosphate on uranium nitrate, but attempts to obtain calco-uranite always result in the formation of  $\text{H}(\text{UO}_2)\text{PO}_4 + 4\text{H}_2\text{O}$ .

L. J. S.

**Pure Platinum Metals of Commerce.** By FRANZ MYLIUS and RUDOLF DIETZ (*Ber.*, 1899, 31, 3187—3193).—A number of ingots of purified platinum metal supplied by the firm of Hereaus of Hanau were analysed with the object of ascertaining the degree of purity attained in the commercial processes of purification. Platinum was not perceptibly impure. Palladium contained at least 99.9 per cent. of pure metal, 0.05 per cent. of platinum being also present. Iridium contained not more than 0.3 per cent. of impurities, of which a trace was ruthenium and 0.15 per cent. platinum. Rhodium was less pure, containing scarcely 98.4 per cent. of the pure metal; impurities were: 1.5 per cent. of iridium, 0.1 per cent. of ruthenium, and a trace of platinum; another specimen, however, contained only 0.4 per cent. of iridium and a third, only 0.05 per cent. of platinum.

The persistence with which iridium adheres to rhodium finds its explanation in the fact that iridium forms a pentammine chloride, isomorphous with rhodiumpentammine chloride, which is the compound used for the purification of the metal in question; the two compounds are only separable, therefore, by frequently repeated crystallisation, that of iridium being the more soluble of the two. The colour of the solution serves as a criterion of the purity of the rhodium compound, as it is colourless when free from iridium; moreover, the impure compound is comparatively readily soluble.

Osmium, hitherto believed to be infusible, may be melted with the help of the electric furnace.

The existence of volatile oxides of osmium and ruthenium renders it easy to obtain these metals in a pure state. Perosmic acid, as sold, is practically pure; perruthenic acid is not sold owing to the readiness with which it undergoes decomposition, but the dioxide may be obtained and converted by fusion with potash and nitre into potassium ruthenate ( $\text{K}_2\text{RuO}_4$ ) and the solution of the latter, after treatment with chlorine, yields the pure tetroxide on distillation.

The paper concludes with the description of a method for the detection of the platinum metals when mixed together in presence of others, including gold and mercury ; the method, however, is lengthy, and does not lend itself to abstraction.

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A. L.

## Mineralogical Chemistry.

**Generalisations on Humous Coal.** By C. EG. BERTRAND (*Compt. rend.*, 1898, 127, 767—769).—The author puts forward a number of generalisations deduced from the microscopic study of specimens of oil shales and bituminous coal. G. T. M.

**Salt on Shore of Lake Ruzsanda.** By ALEXANDER VON KALECSINSZKY (*Földtani Közlemény*, 1898, 28, 234—236, 283—285).—The water of the Lake Ruzsanda, Com. Torontal, Hungary, is yellowish, and has an alkaline taste and a soapy odour; it is used for baths. On the shore of the lake there is a deposit of whitish salt, a sample of which contained 53·32 per cent. of insoluble matter, mainly sand; the soluble portion contained

Na.	K.	Ca.	Mg.	Fe, Al.	SO <sub>4</sub> .	CO <sub>3</sub> .	Cl.	SiO <sub>2</sub> .	H <sub>2</sub> O at 100°.	H <sub>2</sub> O on ignition.	Total.
31·744	0·228	0·100	0·055	traces	60·804	2·490	2·828	0·009	0·338	1·441	100·037

This corresponds with 86·86 per cent. of sodium sulphate, 4·07 of sodium carbonate, and 4·66 of sodium chloride. In efflorescences of this kind from other localities, there is usually much more sodium carbonate. An analysis is quoted of the water of the lake, in which sodium sulphate, carbonate, and chloride are present in about equal amounts. L. J. S.

**Artificial Production of Lautarite.** By AUGUST B. DE SCHULTEN (*Bull. Soc. franc. Min.*, 1898, 21, 144—145).—The mineral lautarite,  $\text{Ca}(\text{IO}_3)_2$ , occurs in the Chilian nitrate deposits (*Abstr.*, 1892, 124). It is prepared artificially by saturating molten sodium nitrate with amorphous calcium iodate,  $\text{Ca}(\text{IO}_3)_2 + \text{H}_2\text{O}$ . The latter is prepared by heating precipitated  $\text{Ca}(\text{IO}_3)_2 + 6\text{H}_2\text{O}$  at 100°. The fused mass contains brilliant, monosymmetric crystals of the composition  $\text{Ca}(\text{IO}_3)_2$ , which are slightly soluble in water, and have the same habit and angles as the natural mineral; sp. gr. = 4·591.

L. J. S.

**Artificial Production of Lanarkite.** By AUGUST B. DE SCHULTEN (*Bull. Soc. franc. Min.*, 1898, 21, 142—144).—Lanarkite is produced by the action of basic lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PbO}$ , on sodium sulphate; when sodium hydroxide is added to a solution of normal lead acetate and the filtrate added to a hot solution of sodium

sulphate, a crystalline precipitate having the composition  $2\text{PbO}\cdot\text{SO}_3$ , is formed; sp. gr. = 6.923. By diffusion, larger crystals, several millimetres in length, can be obtained, together with crystals of anglesite. The colourless, monosymmetric crystals are elongated in the direction of the axis of symmetry, and have the same habit and angles as the natural crystals.

L. J. S.

**Cobalt Deposits at Port Macquarie, New South Wales.** By JOHN B. JAQUET (*Ann. Rept. [1897] Dept. Mines, New South Wales, 1898, 177—180*).—Earthy cobaltiferous wad (asbolite) occurs at Port Macquarie in considerable amount in nests and pockets in serpentine and scattered throughout the red clays which result from the decomposition of the serpentine. It is black to bluish-black (the latter containing more cobalt), with a more or less spongy texture, and a rudely laminated or botryoidal structure. Analysis by H. P. White of a picked sample of ore gave

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{MnO}_2$ .	$\text{CoO}$ .	$\text{NiO}$ .	$\text{Cr}_2\text{O}_3$ .	$\text{CuO}$ .	$\text{CaO}$ .	$\text{MgO}$ .
6.40	9.97	16.85	36.50	7.03	2.39	0.40	0.12	1.20	0.83
		$\text{P}_2\text{O}_5$ .	$\text{CO}_2$ .	$\text{H}_2\text{O at } 100^\circ$ .	$\text{H}_2\text{O combined}$ .		Total.		
		0.14	0.22	5.38	12.24		99.67		

Chrome iron ore is associated with the wad in places. This mode of occurrence is similar to that of the cobalt ores of New Caledonia. The material has probably been segregated during the processes of decomposition of the serpentine.

L. J. S.

[Augite] from Kreuzberg, Rhön Mtns. By E. VON SEYFRIED (*Inaug.-Diss. Strassburg*; and *Jahrb. k. preuss. geol. Landesanst.* [for 1896], 1897, 1—38). The Triassic volcanic rocks of this district in Bavaria are described. Analysis I is of augite (after deducting 4.06 per cent. of magnetite and calculating to 100) taken from tephrite, which gave anal. II.

$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	Loss on ignition.	Total.	Sp.gr.
I 44.15	—	12.11	—	9.16	20.50	9.80	0.85	3.43	—	100.00	3.46
II 53.26	0.31	16.63	8.29	3.21	7.30	1.10	3.54	5.31	1.43	100.38	2.671

Analyses are also given of nephelite-basalt, basanite, and felspar-basalt.

L. J. S.

**Differentiation in Igneous Magmas as a Result of Progressive Crystallisation.** By J. J. HARRIS TEALL (*Rept. Brit. Assoc.*, [for 1897], 1898, 67, 661—662; and *Quart. J. Geol. Soc.*, 1897, 53, 482—488).—Crystal building in a homogeneous igneous magma necessarily produces differentiation into portions of different chemical composition. Usually iron ores are the first, and quartz the last, to crystallise out; but in the basalts of Franz Josef Land, the magnetite is the last to separate, and the mother liquor remaining after the labradorite and augite have crystallised is, therefore, more basic. Analysis of the palagonite representing this basic residue gave

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
35.48	8.30	12.30	14.60	1.04	7.10	3.92	trace	16.80	99.5

The progressive crystallisation has here given rise to a concentration

of iron and of magnesia and a reduction of silica, alumina, and lime in the mother liquor; and in dykes the more basic portion would be in the centre instead of at the margins, as is more usually the case.

The palagonite results from the alteration of brown glass; it is interstitial between the labradorite (sp. gr. = 2.7) and augite, and also fills amygdales in the vesicular basalts. It is a soft, black or greenish-black substance, sp. gr. = 2.4, and is readily attacked by hydrochloric acid, leaving a white, siliceous skeleton. Under the microscope, in very thin sections, it is doubly refracting and appears to be formed of minute interlacing fibres or scales of a brown, or rarely green, substance. In composition, it differs from hullite and other palagonites, in that much of the iron is ferrous. L. J. S.

**Rocks from Franz Josef Land.** By E. TULLY NEWTON and J. J. HARRIS TEALL (*Quart. J. Geol. Soc.*, 1898, 54, 646—651. Compare preceding abstract).—The common type of basalt of wide distribution in Franz Josef Land consists of labradorite, augite, magnetite, rarely olivine, together with interstitial matter and various secondary products. Analysis by Teall gave

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
47.28	1.48	13.24	4.44	10.50	0.40	11.04	5.94	0.31	2.62	2.00	99.25

This agrees very closely with analyses of basalt from Iceland.

L. J. S.

**Water of the Illyes Lake, Hungary.** By BELA LENGYEL (*Földtani Közlöny*, 1898, 28, 229—234, 280—282).—Three lakes in the salt district near Szovata, Com. Maros-Torda, Transylvania, were formed in 1875—9 by subsidences consequent on the removal by springs of material from the salt-bearing strata. The water in these lakes is used for baths; it is very heavy, and has a temperature of 60° at a depth of 3—4 metres. On the surface is a layer of cold, fresh water brought in by streams. 1000 grams of water from the Illyes Lake contains: Na, 91.23003; Ca, 0.60061; Mg, 0.07109; Fe, 0.00622; Cl, 140.70685; Br, 0.00759; SO<sub>4</sub>, 1.01750; CO<sub>3</sub>, 0.09800; SiO<sub>2</sub>, 0.009. Total: 37233.74726 grams.

L. J. S.

## Physiological Chemistry.

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**Temperature of the Human Body.** By MARCUS S. PEMBREY and B. A. NICOL (*J. Physiol.*, 1898, 23, 386—406).—A large number of observations on two healthy men are given. The temperature was usually taken of the stream of urine, which is a trustworthy indication of the internal temperature; the mouth and axilla are not so.

The observations show the diurnal variations of the temperature, but the most prominent feature is the very considerable rise of body temperature that occurs as the result of muscular exercise. Food only causes a slight rise. Mental work has little or no effect.

A simple flat bulb mercurial thermometer gives results which com-

pare favourably with those given by thermo-electric methods of determining the temperature of the skin. W. D. H.

**Influence of Antiseptics on the Artificial Gastric Digestion of Fibrin.** By CHARLES F. MABERY and LEO GOLDSMITH (*J. Amer. Chem. Soc.*, 1897, 19, 889—894).—The substances tested were alum, cream of tartar, boric acid, and formalin. Alum alone exhibits a marked effect in retarding digestion. W. D. H.

**Action of Certain Substances on Digestive Ferments.** By FRANK D. SIMONS (*J. Amer. Chem. Soc.*, 1897, 19, 744—754).—The following substances retard the artificial gastric digestion of proteids: picric acid, tropæolin 000, metanil-yellow. The following retard artificial pancreatic digestion of proteids: bismarck brown, oil of cinnamon, and formol. Gastric digestion ensues only after prolonged treatment if salicylic acid or oil of winter-green is added to the mixture. Both gastric and pancreatic digestion progress normally in the presence of oil of peppermint, chrysoidine, safranine, and methylene-blue. W. D. H.

**Ferment Actions of the Succus Entericus.** By FRIEDRICH KRÜGER (*Zeit. Biol.*, 1898, 37, 229—260).—The bulk of the present paper is occupied with references to past work on the subject of the action of the juice of the small intestine. The remainder describes experiments which confirm the results already well known to physiologists in this country, namely, that the juice does not act on proteids or fats; that it is able to saccharify cooked starch; that it inverts cane-sugar, and has no reverting properties. W. D. H.

**Glycocine as an Intermediate Product of Metabolism.** By HUGO WIENER (*Chem. Centr.*, 1898, i, 626—627; from *Arch. Exp. Path. Pharm.*, 40, 313—325).—If more than 0.7—0.8 gram of benzoic acid per kilo. of body weight is given by the mouth to rabbits, the excess is not excreted as hippuric acid, but as free benzoic acid; the maximum amount of glycocine available for the formation of hippuric acid is, therefore, 0.32—0.34 gram per kilo. of the rabbit's body weight. 1.7 gram of benzoic acid per kilo. is fatal; but if glycocine is injected at the same time, this amount can be considerably exceeded without untoward results. Alanine and asparagine do not act in this way, but leucine does; this amido-acid, therefore, yields glycocine as an intermediate product. Feeding with uric acid increases the amount of urea, and also the hippuric acid excreted. W. D. H.

**Halogen Metabolism.** By F. BLUM (*Chem. Centr.*, 1898, i, 992—993; from *Münch. med. Woch.*, 45, 231—233. Compare Abstr., 1898, i, 287).—Iodothyryn is regarded as an artificial product; it does not occur free in the thyroid. The non-coagulable iodine-containing proteid of that gland is termed *thyrogen*; formaldehyde converts it into a non-coagulable variety called *thyrogen f*. Synthetically prepared iodine compounds of albumin, on treatment with dilute alkalis, or on gastric digestion, yield a product of which the properties are similar to those of iodothyryn. After feeding on the iodine-containing substance of the thyroid, potassium iodide appears in the urine; this



is supposed to be formed by oxidation in the body leading to the appearance of nascent iodine. W. D. H.

**Formation of Urea from Oxamic Acid in the Organism.** By LEO SCHWARZ (*Chem. Centr.*, 1898, i, 951; from *Arch. Exp. Path. Pharm.*, 1898, 41, 60—73).—Only a small part of the oxamic acid given passes from the body as urea, and there is no formation of oxalic acid; the greater part of the oxamic acid passes unchanged into the urine. Minced liver has not the power to change oxamic acid into urea. W. D. H.

**Properties and Formation of Lymph.** By LEON ASHER (*Zeit. Biol.*, 1898, 37, 261—306. Compare Abstr., 1898, ii, 239).—Intravenous injection of bile increases the activity of the liver, and causes an increased flow of concentrated lymph from the thoracic duct; this confirms the views previously expressed by the author. After a time, this lymph contains hæmoglobin, but the fluids in the serous cavities and the urine contain no hæmoglobin. This is in favour of the view that the fluids in the serous cavities are not the same as tissue-lymph; possibly they are secretions. Urea which does not plasmolyse blood-corpuscles, like sugar and sodium chloride which do, causes an increase of lymph.

Sometimes the intravenous injection of small quantities of crystalloid materials causes a noteworthy rise in the percentage of solids in the lymph; this cannot be a mechanical result, but is due to the increase in metabolism which is thus set on foot.

Choline causes no increase in bile formation; the lymph also is not more concentrated; but the amount of lymph in the neck and thoracic lymphatics is increased, which corresponds with the fact that choline stimulates secretion in glands. Muscarine behaves in the same way.

Simultaneous injection of crystalloid substances and choline causes little or no lessening of the concentration of the lymph.

The results of the intravenous injection of crystalloid substances are thus partly due to physical, partly to physiological factors.

W. D. H.

**Action of the Cells of Frog's Lymph on Bacilli.** By W. B. HARDY (*J. Physiol.*, 1898, 23, 359—375).—Measurements show that contact with an oxyphile cell of frog's lymph retards or stops the growth of a chain of *Bacillus filamentosus*. Below 19°, growth is arrested, whilst between 20° and 25° it is only retarded. The cells exert the action by coating the chain with a slime derived from the oxyphile granules. Contact with a hyaline cell, on the other hand, does not necessarily have any effect on the growth of the bacilli, but if the bacillus gets enclosed within vacuoles developed in the cell-substance, then retardation of growth occurs.

W. D. H.

**Thiocyanic Acid in Human Saliva.** By FRIEDRICH KRÜGER (*Zeit. Biol.*, 1898, 37, 6—24).—The quantity of saliva secreted by a man in the 24 hours varies between 250 and 300 c.c., and is not influenced to any important degree by cigarette smoking.

Thiocyanic acid is a normal constituent of the saliva, and is not produced by putrefactive processes, nor by foreign admixture due to smoking. The amount present is independent of age, sex, health, or disease; the saliva of smokers, however, contains two or three times as much as that of non-smokers.

W. D. H.

**The Number of Red and Colourless Corpuscles and Amount of Hæmoglobin at Different Ages in Man.** By WILHELM SCHWINGE (*Pflüger's Archiv.*, 1898, 73, 299—338).—After birth, the quantity of red corpuscles and of hæmoglobin are at their maximum; these two values soon sink to a minimum, rise during growth, and during adult life show periodic alterations, finally sinking once more towards the end of life. The number of colourless corpuscles behaves in the reverse manner, sinking during growth and adolescence, and rising afterwards. The two sexes differ in that, during puberty, the numbers for the female sex are smaller than those for the male. The differences noted are believed to be parallel to differences in metabolic activity, and correspond with the amount of interchange between blood and tissues. The high percentage of leucocytes in youth illustrates the formation of new formed elements at that period of life. W. D. H.

**Comparative Physiology of Digestion. II. Presence of an Enzyme which Dissolves Cellulose in the Secretion of the Liver of the Snail (*Helix pomatia*).** By WILHELM BIEDERMANN and P. MORITZ (*Pflüger's Archiv*, 1898, 73, 219—287. Compare Abstr., 1898, ii, 614).—That cellulose is digested in the alimentary canal of many animals is an undoubted fact; in most instances, this is believed to be due to the action of micro-organisms, and although the existence of an enzyme which has the same power has been mooted by several observers, their results can hardly be considered as definite; on the other hand, in the vegetable world, the existence of a 'cytase' appears in many cases to be have been satisfactorily proved. The first part of the present paper is occupied with a lengthy critical discussion of these results.

The secretion of the so-called liver of the snail, *Helix pomatia*, is remarkably rich in proteid material; it converts starch into dextrose, but its most marked characteristic is the possession of a very active cytase, which acts, not only on the more soluble constituents of the cell wall, like the hemicelluloses, but on the more insoluble materials also which have not undergone actual conversion into woody fibre. The products of action on the hemicelluloses are the same as those which are produced by the action of dilute mineral acids on those substances. The secretion was collected from the intestinal canal of the animals; extracts of the liver have no action on cellulose; doubtless, the cytase is preceded in the liver cells by a zymogen, which is not converted into the enzyme during the process of extraction. The ferment resembles that described in the secretion of the crab's 'liver' by acting at a low temperature. The reaction of the juice has been described by some previous observers as markedly acid; this is not so, the acid reaction which can be demonstrated with some indicators is slight, and is due to acid salts; the juice is alkaline to litmus and to lacmoid. The juice has no action on proteids; numerous proteids of both

animal and vegetable origin were tried ; the observations were made between April and September, but it is possible that at other periods of the year its action may be different.

W. D. H.

**Fate of Hæmoglobin in the Organism.** By SCHURIG (*Chem. Centr.*, 1898, i, 951 ; from *Arch. Exp. Path. Pharm.*, 1898, 41, 29—59).—Injection of 0.5 gram of hæmoglobin per kilo. of body weight in rabbits for 17 days does not lead to hæmoglobinuria, but this condition appears in 6 days after a daily injection of 1 gram. Hæmoglobin is also found in the bile. The urine is dark, but does not contain bile pigment. After the injection, the connective tissues are rich in iron ; part of the hæmoglobin is changed into bilirubin by the liver, and part is found in the spleen and bone-marrow as iron compounds, which can be detected microchemically.

W. D. H.

**Action of Arsenic on Bone Marrow and Blood.** By RALPH STOCKMAN and E. D. W. GREIG (*J. Physiol.*, 1898, 23, 376—382).—In healthy animals, arsenic does not increase the number of blood corpuscles nor the amount of hæmoglobin. In pernicious anæmia, it acts favourably by stimulating the red-marrow ; it does not, however, affect the real cause of the disease, and is simply a symptomatic method of treatment.

W. D. H.

**Action of Copper on the Animal Organism.** By HERM. BAUM and RICHARD SEELIGER (*Chem. Centr.*, 1898, i, 852 ; from *Zeit. öffentl. Chem.*, 4, 181—210).—Different preparations of copper have different degrees of toxicity, copper oleate being by far the most poisonous of the compounds investigated ; then follow in order, copper acetate, copper sulphate, and "cupro-hæmol" ; the last-named has little or no harmful action. The toxic action is mainly on the brain and on metabolism.

W. D. H.

**Physiological Action of Alkalis and Acids when greatly Diluted.** By JACQUES LOEB (*Pflüger's Archiv.*, 1898, 73, 422—426).—It is well known that the activity of spermatozoa and cilia is increased by dilute alkalis ; to say that the alkali acts as a stimulus is no real explanation of this fact. Investigations were undertaken to discover whether the stimulus acts by increasing oxidation processes in the living cilia. The infusorian *Paramœcium* was selected for experiment. These animals were divided into three sets—one in distilled water, one in distilled water to which a little alkali was added, and the third in distilled water to which a little acid was added ; all were placed in an Engelmann's chamber, and a stream of pure hydrogen passed through it. Those in the alkaline solution lived longest ; the dilution of the sodium hydroxide employed must be from  $\frac{1}{1200}$  to  $\frac{1}{1800}$  per cent. ; greater dilution gives a negative result, less dilution hastens the death of the *Paramœcium*. Acids in every degree of dilution are very fatal.

In fever, the alkalinity of the blood decreases ; whether this is related to the metabolic activity of the febrile state is uncertain, but it is certainly the case that *Paramœcium* lives and moves longer at a temperature of 40° in an alkaline than it does in a neutral or acid solution.

Potassium cyanide kills by preventing the assimilation of oxygen (C. Bernard and Geppert); a trace of alkali, however, added to a fatal solution of this salt prolongs the life of the *Paramæcium* considerably. The same is true for atropine, but veratrine and strychnine are equally fatal in acid, neutral, and alkaline solutions.

Another series of experiments were performed with the larvæ of the sea-urchin. According to Hoppe-Seyler, free oxygen is necessary for embryonic development; in the present research, dilute alkali was added to see if the development and growth of the larvæ were hastened; this was found to be so in a marvellous degree. From such experiments it is inferred that dilute alkalis favour, dilute acids impede, oxidation in the living organism. It is recommended that in transfusion, after severe hæmorrhage, a dilute alkaline solution should be used. Another practical issue appears to be the desirability of administering alkalis in fevers.

W. D. H.

**Chloride Metabolism in Pneumonia and Acute Fevers.** By ROBERT HUTCHISON (*J. Pathol. and Bacteriol.*, 1898, 5, 406—442).—The research confirms the old statement that during an attack of croupous pneumonia the chlorides of the urine are greatly diminished, or may even entirely disappear. There is a true retention of about 2 grams per diem within the body. This lasts until one or two days after the crisis, and is succeeded by an excessive secretion of chlorides. The degree of diminution varies, but has no relation to the intensity of the fever, lung trouble, or to concomitant albuminuria. The phosphates, sulphates, and urea are increased. Decrease of chlorides may occur in other fevers, such as typhus and acute rheumatism, whilst in malaria the chlorides are increased. The presence of abundant chlorides would negative the diagnosis of pneumonia, but diminution of chlorides is not pathognomonic of that disease.

The absorption of chlorides goes on normally in acute fevers, and no vicarious excretion occurs; there is, however, some increase of these salts in the sputum and in the inflammatory exudation. There is no functional disability of the kidneys to explain the decrease in the urine. The chlorides of the blood are lessened, but there is an increase in all the organs and fixed tissues in general, not in any one in particular. Attempts to produce chloride retention in pyrexia by injection of the pneumococcus failed. Views on the cause of the retention of the chlorides are merely speculative, but are discussed fully; it does not appear to be the result of a retention of water.

The increased secretion of chlorides in malaria is due to increase of arterial pressure in the kidney during the pyrexial stage of that disease.

W. D. H.

**Influence of Experimental Jaundice on the Glycogen of Liver and Muscles.** By FRIEDRICH VON REUSZ (*Chem. Centr.*, 1898, i, 950—951; from *Arch. exp. Path. Pharm.*, 41, 19—28).—By feeding rabbits on sugar after ligature of the bile ducts, it is found that the sugar is badly absorbed, and, *post mortem*, much is found in the subcutaneous tissues; nevertheless, there are considerable quantities of glycogen in the liver and muscles. Slight diuresis and glycosuria generally occur. Diabetic puncture in these animals causes only slight

glycosuria. There is a good deal of fermentative change in the sugar in the alimentary tract. In dogs, ligature of some branches of the bile duct leads to an increase of water, but only to a slight lessening of the glycogen in the icteric portions of the liver. W. D. H.

**Chemico-physiological Studies on Phloridzin.** By MAX CREMER (*Zeit. Biol.*, 1898, 37, 59—81. Compare Abstr., 1898, ii, 243).—Of all theories on phloridzin diabetes, the original one of von Mering is the most probable; still a true secretory activity has also to be taken into account. There is no evidence of any increased new formation of dextrose molecules, and it is possible, but not proved, that the rise in the sugar of the blood is due to the dextrose molecules preformed in glycogen. Phloridzin has no special influence on the cells of the mammary gland, in spite of what Cornevin (*Compt. rend.*, 116, 263) says to the contrary. W. D. H.

**Di-iodacetylidene as a Poison.** By OSCAR LOEW (*Zeit. Biol.*, 1898, 37, 222—228).—According to Nef, the substance obtained by the action of iodine on silver acetylde is not di-iodacetylene, but the isomeric di-iodacetylidene,  $C_2Cl_2$ . In keeping with this view, the experiments recorded show the intensely poisonous character of this substance to all kinds of animal and vegetable life. A solution of 1 part in 20,000 kills bacteria, moulds, and yeasts. Solutions of 1 in 100,000 kill algæ in a few hours, of 1 in 1,000,000 in a few days. Similar results were obtained in other cases; the amount of dilution necessary varies, but is always very high; these cases include infusoria, flagellata, copepods, nematodes, rotifers, &c. In vertebrate animals, the substance was breathed in the form of vapour, or injected under the skin; here again the small toxic dose is equally remarkable.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Importance of Stereo-chemistry in Physiology.** By EMIL FISCHER (*Zeit. physiol. Chem.*, 1898, 26, 60—87).—The object of this paper is to bring before physiologists the bearing of the author's work, especially on the carbohydrates. Such importance is indicated by the way in which isomerides are affected by micro-organisms and fungi, some being destroyed, and other substances, with a different optical action, being unaffected.

W. D. H.

**Relation of Oxygen to the Activity of Living Yeast-cells.** By HANS BUCHNER and RUDOLPH RAPP (*Zeit. Biol.*, 1898, 37, 82—142).—An abundant oxygen supply has no really favourable influence on the fermentative activity, as such, of yeast-cells; it leads to an increase in their number, but the gas is as indifferent as hydrogen or nitrogen is towards the ferment-process as such, that is, towards the formation of zymase. Only in pure surface cultures (on sugar-gelatin) is there an increased respiratory decomposition of

the sugar by the yeast-cells, accompanied by increased fermentative activity. Mechanical shaking of the yeast-cells beyond a certain point has a harmful influence on them. Zymase is the only active agent in the chemical changes produced by yeast.

W. D. H.

**Composition of Buchner's Yeast Extract.** By AUGUSTIN WROBLEWSKI (*Ber.*, 1898, 31, 3218—3225).—The proteid substances include invertase and a proteolytic ferment (*Abstr.*, 1898, ii, 246), both of which are probably contained in the same precipitates from the extract as are the proteoses. No ferment capable of decomposing starch could be detected, and the presence of oxydases has not been established with any certainty. The presence of several coagulable proteids has been established by the process of partial coagulation; these separate at 40°, 51°, 56°, 59°, 62°, and 68° respectively. The first proteid is also coagulated by ether at 35°, and does not pass through a Chamberland filter; it seems to be the one which most readily undergoes alteration when the extract is kept. Attempts at fractional salting out with concentrated ammonium sulphate (3.8 c.c. of extract to 6.2 c.c. of sulphate solution) indicate that the proteids which coagulate above 60° are precipitated, whilst the others remain in solution. A complex carbohydrate, small amounts of proteoses, and larger quantities of peptone, and a substance with reducing properties have also been isolated. Tyrosin, leucine, glutamic and other amido-acids, together with glycerol, are contained in the alcoholic filtrate from the peptones.

J. J. S.

**Action of the Sorbose Bacterium on Aldoses.** By GABRIEL BERTRAND (*Compt. rend.*, 1898, 127, 728—730. Compare *Abstr.*, 1898, i, 530 and 536, and this vol., ii, 44).—When the sorbose bacterium is cultivated in a yeast decoction containing an aldose, it is found that after a time a portion of the sugar has disappeared, whilst a corresponding amount of a monobasic acid has been produced. Three solutions containing 5 grams of arabinose, dextrose, and galactose yielded, after 25 days, 0.74 gram of arabonic acid, 1.27 grams of gluconic acid, and 3.62 grams of galactonic acid respectively.

G. T. M.

**Action of Ammonium Salts on *Aspergillus Niger*.** By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 914—921. Compare *Abstr.*, 1897, ii, 154 and 338).—The author has already shown that when *Aspergillus niger* is sown in a nutrient solution containing an excess of ammonium nitrate, the mycelium can be made to grow continuously without the formation of spores during as long a period as a month, provided the solution is renewed every day; if, however, this liberal diet is curtailed, or if the temperature is allowed to fall much below 30°, fructification at once sets in. It is now shown that a similar effect is produced by ammonium sulphate and ammonium chloride; on the other hand, ammonium phosphate appears to favour the production of spores. The growth of the mycelium, of which 200 grams can be obtained in 10 days from 400 sq. cm. of surface, is accompanied by the liberation of mineral acids, the ammonia only of the ammonium salts being absorbed by the fungus; the author,

therefore, suggests that the large excess of mineral bases in the ash of plants is due to a similar absorption of the bases of the neutral salts, whilst the acids are excreted. Starch is formed in considerable quantities under the conditions described, although it does not appear in ordinary cultures; the quantity, estimated by a colorimetric method, was found to be nearly 5 per cent. of the weight of the mycelium under favourable conditions; traces of starch were also found in the nutrient liquors, together with larger quantities of dextrin and dextrose. When rendered soluble by the action of acids and purified by precipitation with baryta, the starch from *A. niger* gave  $[\alpha]_D = +177^\circ$ , whilst ordinary starch gave  $[\alpha]_D = +185^\circ$ ; its identity was further established by conversion into dextrose.

When nourished with racemic inositol instead of cane-sugar, the mycelium growth of *A. niger* did not effect the resolution of the optical isomerides, but in ordinary cultures the dextrorotatory form was consumed more rapidly, the liquid in which fructification had taken place becoming levorotatory.

T. M. L.

**Fungi.** By CHARLES TANRET (*Bull. Soc. Chim.*, 1897, [iii], 17, 921—927).—When *Aspergillus niger* is macerated successively with water, alcohol, ether, and 5 per cent. caustic soda, and then digested with dilute sulphuric acid at  $100^\circ$  for several hours, an insoluble residue of “fungin” remains. By treating this product a second time with caustic soda (2 per cent.), the author has obtained a residue of pure chitin; the identity of this substance was established by analysis (C = 46.28, H = 6.63, N = 6.30), and also by the formation of glucosamine on heating with hydrochloric acid at  $100^\circ$ , and of chitosan on heating with potash at  $170^\circ$ . Other fungi gave similar results, but in no case was a residue of pure chitin obtained; thus, the chitin of the crab and that from *A. niger* gave 82.5 per cent. of glucosamine hydrochloride, but the residue from *Claviceps purpurea* gave only 47.0 per cent., that from *Polyporus officinalis* gave 40.8 per cent., and that from *Boletus edulis* 39.5 per cent.; yeast, on similar treatment, gave only a minute quantity of insoluble residue, and may, therefore, be regarded as practically free from chitin.

The author applies the name *fungose* to that part of the crude fungin which is soluble in soda; these substances approximate to cellulose in composition, but contain a small and variable percentage of nitrogen; they do not, however, dissolve in Schweitzer's reagent, and give no blue coloration with iodine after treatment with sulphuric acid. Like cellulose, they dissolve slowly in 90 per cent. sulphuric acid and are converted into glucose ( $[\alpha]_D = +50^\circ$ ); by the action of acetic anhydride and sodium acetate, they give di- and tri-acetates which are levorotatory, whilst the salts are dextrorotatory; they are insoluble in ammonia. The author has examined the fungoses from *A. niger*, *C. purpurea*, *P. officinalis*, and also that from *Saccharomyces cerevisiae* which has been previously mistaken for cellulose.

T. M. L.

**Change in Composition of Oleaginous Seeds during Germination.** By LÉON MAQUENNE (*Compt. rend.*, 1898, 127, 625—628).—It is well known that the germination of many oleaginous seeds is



accompanied by an increase in the amount of sugar present, and a decrease in that of the fats; in order to determine whether sugar is elaborated, during this change, from the acid radicle of the fat, and, if so, whether the nature of the latter influences the result, the behaviour, during germination, of seeds of *Arachis* (earth nut) and *Ricinus* (castor oil seed) was studied. The former contains the saturated fatty acid, arachidic acid, whilst the latter contains the unsaturated ricinoleic acid. The seeds were grown in sand at 20–25°, complete analyses being made at different stages of the plant's growth. The results obtained indicate that the amount of oil decreases in both kinds of seed during the whole period of germination; the maximum increase of total carbohydrates present, including "cellulose," occurs after 18 days in the case of *Arachis*, and after 10 days in that of *Ricinus*. In the first case, the increase is 5·6 per cent., and in the second 16 per cent.; the former appears entirely attributable to the glycerol of the oil being transformed into sugar, but the latter involves a transformation of the ricinoleic acid into carbohydrates. The term "cellulose" used by the author denotes that portion of the plant which remains after successive treatment with light petroleum, dilute sulphuric acid, and 10 per cent. caustic potash; it contains, in addition to true cellulose, insoluble substances richer in carbon, which are sometimes nitrogenous. The sugar formed appears to consist principally of glucose, associated, perhaps, with levulose. In the case of *Arachis*, there is an initial decrease in its amount, with a subsequent increase, whilst in the case of *Ricinus*, a very rapid increase first occurs, followed by an equally rapid decrease; in the former case, the increase of "cellulose" is continuous, whilst in the latter it is preceded by a decrease. The amount of nitrogen present undergoes little change.

Generalising from his results, the author considers that the fatty acids are less readily transformed into sugars than acids of the oleic series, and probably take part only in respiratory functions. The change of unsaturated acids, and especially of ricinoleic acid, into sugar, probably depends on the presence in the centre of the acid chain of the allyl grouping,  $\text{CH}:\text{CH}\cdot\text{CH}_2$ ; this is liberated by the progressive combustion of the ends, and gives rise, initially, to glycerol, which subsequently undergoes polymerisation. W. A. D.

**Absorption of Haloid Potassium Salts by Plants.** By E. DEMOUSSY (*Compt. rend.*, 1898, 127, 771–774).—Terrestrial plants whose roots are immersed in solutions of potassium nitrate or potassium chloride absorb these salts at equal rates (compare Abstr., 1896, ii, 128), and the nitrate or chloride, when once absorbed, is retained by the living protoplasm, so that it cannot be extracted with cold water. Boiling water removes the salt, and the same result is obtained by first killing the plant with ether and then extracting with cold water. Potassium chloride is of far less importance to the plant than potassium nitrate, yet each is absorbed with equal readiness; potassium bromide, which is never found in terrestrial plants, is also taken up by them in a precisely similar manner, when their roots are immersed in its solution. In the case of these three salts, the amount removed from solution by the plant is far greater than that which would have

been absorbed owing to transpiration. With potassium iodide, the result is quite different; absorption keeps pace exactly with transpiration, and the salt exerts a toxic effect on the plant. The behaviour of the terrestrial plant towards iodine is contrasted with that of the marine flora, in which this element is an essential constituent of the vegetable tissues. G. T. M.

**Absorption of Carbohydrates by Roots of Plants.** By JULES LAURENT (*Compt. rend.*, 1898, 127, 786—787).—Seedlings of maize, when surrounded by an atmosphere deprived of carbonic anhydride, and cultivated in sterilised solutions containing glucose, continue to grow, and after a few weeks exhibit a considerable increase in the weight of dry matter; a duplicate culture, made without glucose and placed under the same bell-jar, shows no appreciable change in weight. The presence of sunlight is beneficial, the increase of weight being less when the plant in the glucose solution is cultivated in the dark. Other carbohydrates, such as cane sugar, dextrin, or starch can be utilised by the plant; the roots have a powerful inverting action on the former, whereas the absorption of dextrin or starch is very slow. The seedlings of various plants, developed in distilled water until their reserve material is exhausted, and deprived of starch by cultivation in the dark, are immersed in glucose solutions surrounded by an atmosphere free from carbonic anhydride, and allowed to remain in sunlight during 5 or 6 hours at a temperature of 20—25°; at the end of the time, the leaves are found to contain a notable amount of starch. These experiments indicate that the glucose absorbed by the roots is utilised by the plant in the synthesis of starch, and that green plants assimilate carbon, not only by the agency of chlorophyll, but also by the absorption of certain carbohydrates by their roots.

G. T. M.

**Assimilation of Nitrogen as Ammonia and Nitrites by the Higher Plants.** By LAURENT, EM. MARCHAL, and CARPIAUX (*Bied. Centr.*, 1898, 27, 821—823; from *Bul. Acad. Belg.*, 1896, 32, 815—865, and *Bot. Centr.*, 1897, 70, 232).—The object of the experiments was to ascertain whether, in the case of higher plants, the presence of light is necessary to enable ammonia and nitric nitrogen to be assimilated.

Various plants were kept, with and without light, in distilled water, and in ordinary nutritive solutions containing ammonium sulphate and potassium nitrate respectively, and pure saccharose (4 per cent.). The organic nitrogen, and the nitrogen as ammonia and as nitrates, were determined after several days.

It was found that assimilation only takes place in presence of light. Leaves free from chlorophyll assimilate ammonia vigorously, but not nitrates to any extent; with chlorophyllous leaves, the reverse is the case.

Assimilation of nitrogen depends entirely, or almost entirely, on the ultra-violet rays; when the light passed through a 0.2 per cent. solution of quinine sulphate, assimilation of nitrogen ceased.

N. H. J. M.

**Degeneration of Cattleya.** By ALEXANDRE HÉBERT and GEORGES TRUFFAUT (*Bull. Soc. Chim.*, 1897, [iii], 17, 712—718).—*Cattleya*, when grown under the usual artificial conditions, quickly becomes less vigorous, and in the course of a few years no longer affords saleable blossoms. The authors have compared the composition of plants grown under natural and under artificial conditions, before and after flowering, as well as that of the blossoms themselves. The cause of the degeneration seems to lie in the fact that the flowers contain a higher proportion of nitrogen, phosphorus, calcium, and magnesium than does the rest of the plant, and, in consequence of this, the necessary amount of these constituents in the plant diminishes rapidly with the successive flowering, as they are not supplied by the sphagnum and polypody on which the orchid is usually grown. A. L.

**Phosphoric Acid in Barley and Malt: Presence of Organic Acids in Malt.** By CHARLES G. MATTHEWS and G. H. WOOLCOTT (*J. Fed. Inst. Brew.*, 1898, 4, 6—20).—The authors find that there is a rough relationship between the soluble phosphates of malt and the acidity of the extract, a high acidity as a rule accompanying a high percentage of soluble phosphates; for the estimation of the latter, the malt extract is evaporated to dryness with some lime, the residue charred, and the phosphoric acid determined by the molybdate method. In determining the acidity of malt worts, rosolic acid and litmus give practically the same results, but phenolphthalein gives values which are often four or five times as high, since it is not affected by the secondary phosphates, which are alkaline to rosolic acid; phenolphthalein is, therefore, to be preferred. The authors confirm Prior's statement that there is no connection between the acidity of malt and the total phosphoric acid. Numbers are given showing the percentages of calcium and magnesium in cold-water extracts of malt and in worts.

By extracting malt with alcohol, the authors only obtained 0.024 per cent. fixed acidity and 0.0054 per cent. volatile acidity, calculated in both cases as lactic acid. Butyric, lactic, and succinic acids were identified in the extract. There can, therefore, be no doubt that the acidity of malt is almost entirely due to the presence of acid salts, as Fernbach and others have suggested. A. C. C.

**Carbohydrates of Barley and Malt with special reference to the Pentosans.** By BERNHARD TOLLENS (*J. Fed. Inst. Brew.*, 1898, 4, 438—454).—The author reviews the present state of knowledge in connection with the nature of those carbohydrates of barley and malt which yield pentoses and furfuraldehyde on boiling with dilute acid. He is of opinion that in addition to pentosans, the furfuraldehyde-yielding substances of malt contain other compounds which are more susceptible of fermentation than arabinose and xylose, and which do not contain the methylene group, as suggested by Cross and Bevan, since they do not give the characteristic reaction with phloroglucinol and hydrochloric acid. A. C. C.

**Composition and Feeding Value of French Haricots.** By BALLAND (*Compt. rend.*, 1898, 127, 532—534).—The author has

analysed haricots grown in sixteen departments of France in the year 1897. The mean weight of 100 beans varied from 23·80 to 98·70 grams, and the percentage of husk varied between 6·2 and 9·2. The extremes of composition in the natural state were: water, 9·00 to 14·40; nitrogenous matter, 17·02 to 22·70; fat, 1·10 to 1·90; sugar and starch, 52·22 to 62·56; cellulose, 2·15 to 6·65; ash, 2·25 to 6·65; or in the dry state, nitrogenous matter, 19·61 to 25·80; fat, 1·26 to 2·16; sugar and starch, 61·00 to 71·52; cellulose, 2·50 to 7·57; ash, 2·61 to 7·77.

If the haricots are to be kept for a long time, they must not contain more than 12 to 14 per cent. of water when gathered, and must only be harvested during dry weather. The smaller varieties are generally more nitrogenous, and lose their excess of water more quickly, than the larger beans.

C. H. B.

**Nitric Nitrogen produced by the Pea.** By JASPER L. BEESON (*J. Amer. Chem. Soc.*, 1898, 20, 793—795).—Samples of soil were taken from small plots, on which various plants were growing, at the end of September, after about six weeks of dry weather, and the nitric nitrogen determined. The following amounts of nitrogen per million of soil were found.

Fallow.	Peas (1).	Peas (2).	Peas (3).	Maize and peas.	Maize.	Cotton.	Sorghum.
1·01	3·33	8·67	10·51	7·50	0·34	0·42	0·33

Peas (1) had pods nearly grown, (2) had pods nearly ripe, and (3) had been dead two or three weeks. The cotton and sorghum were still growing, but not the maize.

It is concluded that the nodule bacteria assimilate more nitrogen than the plant requires, and that peas growing with another crop would tend to increase the yield of that crop, provided that they were not too thick to check the root development, or use up too much soil moisture. It is suggested that the nodule bacteria may possibly continue to assimilate nitrogen after the death of the plant as long as there are any juices left in the plant.

The soil was a very productive, rich bottom land. N. H. J. M.

**Nitrification in Soils.** By TH. SCHLÖESING, jun. (*Compt. rend.*, 1897, 125, 824—827).—Whilst the fact that nitrification is less vigorous in heavy than in light soils is usually attributed to insufficient aëration, the author's experiments indicate that, in many cases, at any rate, it is not a deficiency of air but of water which retards nitrification.

Artificial soils, to which ammonium sulphate was added, were kept in flasks for  $2\frac{1}{2}$ — $3\frac{1}{2}$  months, and the nitric nitrogen determined. The sand and clay together amounted in each case to 100 grams. In the following summary, the amount of sand is given (in grams), and the percentage amounts of nitrogen which was nitrified. The chalk which was added was 0·5 gram (Nos. 1—5 and 12—15), and 1·0 gram (6—11). Flasks 1—5 had 0·05; 6—11, 0·1; and 12—15, 0·0666 gram of ammonium sulphate.

No.	Sand.	Water.	N. nitrified	No.	Sand.	Water.	N. nitrified	No.	Sand.	Water.	N. nitrified
	Grams.	Grams.	Per cent.		Grams.	Grams.	Per cent.		Grams.	Grams.	Per cent.
1.	100	10·0	83·0	6.	100	9·5	63·0	12.	70	10·6	80·0
2.	90	10·0	94·0	7.	90	9·5	66·0	13.	70	11·5	100·0
3.	80	10·0	89·0	8.	85	9·5	94·0	14.	70	13·2	100·0
4.	75	10·0	56·0	9.	80	9·5	100·0	15.	70	14·0	100·0
5.	70	10·0	10·0	10.	75	9·5	21·0				
				11.	70	9·5	2·7				

In Nos. 1 and 6, nitrification was incomplete, nitrous acid being present; 9·5 to 10 per cent. of water is probably too much for pure sand, and by occupying too much space hindered aëration.

The very incomplete nitrification in Nos. 4, 5, 10 and 11 could not have been owing to want of air, as the soils were, in each case, quite permeable; moreover, in Nos. 13—15, which contained 30 per cent. of clay, and more water, the whole of the ammonia was nitrified. The failure in the cases mentioned must therefore be ascribed to insufficient water in presence of 25—30 per cent. of clay. With regard to the remarkable effect brought about by a slight increase in water or a slight decrease in clay, it is suggested that the conditions under which nitrification was diminished were owing to the limit having been exceeded, below which the capillary attraction, which retains the water and dissolved substances on the soil, become, nearly everywhere, superior to the osmose which caused the water to penetrate the cells of the microbes, and thus rendered them unable to obtain food from the soil. The results have an important bearing on the question of nitrification in heavy soils.

N. H. J. M.

**Humates and Soil Fertility.** By E. F. LADD (*J. Amer. Chem. Soc.*, 1898, 20, 861—867).—The following summary gives the lowest, highest, and average percentage results obtained with 24 North Dakota soils.

	In soil (total).						In Humus.			
	Humus.	ates.	N.	K <sub>2</sub> O.	CaO.	P <sub>2</sub> O <sub>5</sub> .	N	K <sub>2</sub> O.	CaO.	P <sub>2</sub> O <sub>5</sub>
Lowest .....	3·84	1·56	0·180	0·18	trace	trace	0·041	0·075	0	0·086
Highest .....	15·26	7·90	0·456	0·73	2·70	0·40	0·362	0·233	1·03	0·199
Average .....	9·15	4·77	0·292	0·409	0·944	0·269	0·163	0·153	0·436	0·138

Assuming the weight of an acre of soil to the depth of 1 foot to be 2,225,000 lbs., the total nitrogen will amount, on the average, to 6,497 lbs., the nitrogen in humus to 3,627 lbs., and the phosphoric acid to 5,985 and 3,061 lbs.

As regards the effect of continuous cropping on soils, ordinary analyses of new, unbroken prairie soil and the soil of an adjoining field which had been cropped 17 years (chiefly wheat) gave very little indication as to the cause of the marked decrease in produce which was observed. The amount of humus was found to be unusually low for North Dakota (2·53 per cent.), and by continuous cropping it had been reduced by 39 per cent.

A field which had been cropped continuously for 15 years (wheat) was afterwards rendered more fertile by a system of crop rotation. During 8 years of rotation, the humus increased 46·9 per cent., whilst the phosphoric acid in the form of humates increased 48 per cent.

N. H. J. M.

**Efficacy of Various Manures.** By H. STEFFECK and MAX MAERCKER (*Jahrb. agrik.-chem. Versuchs-Stat. Halle a-S.*, 1896, 2, 105—131).—*The Nitrogen and Phosphoric Acid of Fish Guano.*—Two different Norwegian fish guanos were employed for the experiments, containing N = 11·81 and 9·27, and  $P_2O_5$ , 4·51 and 12·06 per cent. respectively. With both barley and oats, the more nitrogenous guano gave much the best results. In the case of barley, the yield was almost as great as when the same amount of nitrogen in the form of nitrate was given, whilst the barley produced was less nitrogenous. The low percentage of fat in the guano (1·77—1·84 per cent.) was favourable. As regards the effect of the phosphoric acid, it was found to be about equal to 60—70 per cent. of phosphoric acid soluble in water for the first crop.

*Ammonium and Potassium Phosphates.*—As a nitrogenous manure, ammonium phosphate acted in a manner quite similar to ammonium sulphate with both oats and barley, both as regards yield and nitrogen-content of the grain. The effect of the ammonium salt as a phosphate corresponded with only 88·33 per cent. of that of phosphoric acid soluble in water, whilst potassium phosphate was exactly equivalent to a super-phosphate.

*Bone Meal.*—The bone meal was treated with only sufficient sulphuric acid to combine with the calcium present as carbonate, and to form di-calcium phosphate. As a manure, the product equalled, the first year, phosphoric acid soluble in water, and the after effect was greater than that of basic slag. It is thus possible to obtain an excellent manure from bone meal at a slight expense. Four manufactured products contained total  $P_2O_5$ , 19·17—24·25;  $P_2O_5$  soluble in water, 2·10—5·44;  $P_2O_5$  soluble in citrate (excluding soluble in water), 9·80—20·25 per cent.

*Stone Meal.*—The phosphoric acid of stone meal was found to be entirely without effect. The potash is quite insufficient for a crop, even with an application of 100 cwt. per hectare, whilst smaller amounts are injurious, as they induce a certain amount of development in the plants which cannot be maintained.

*Effect of Extracting the Fat from various Nitrogen Manures.*—The manures were meat meal, fish meal, and poudrette. In the case of meat meal, the result of removing the fat was to increase the manurial effect by 17·1 per cent., whilst 16·3 per cent. more nitrogen was taken up by the plants (white mustard). With fish meal, the effect was almost as great as regards the increased amount of nitrogen assimilated. In the case of poudrette, the yield was raised only 5·7 per cent., and the nitrogen taken up was increased by 7·2 per cent. Fish meal, freed from fat, was found to be equivalent to 81·6 per cent. of the value of nitrate, and meat meal to 73·1 per cent. of nitrate. The effect of the residue on the second crop was very slight.

*Various Nitrogenous Manures.*—A process has been proposed for

converting nitrogenous refuse, such as hair, leather, and wool, &c., into a satisfactory manure, by heating 500 parts with a solution of potash (50 parts) containing lime (50 parts) in thin layers, first in a current of carbonic anhydride and afterwards in steam. Slaughter-house refuse thus treated gave very satisfactory results with oats, and especially with barley, whilst refuse from tanned skins gave still better results. Leather refuse was unsatisfactory.

Experiments made with some new guanos are also described.

N. H. J. M.

**Proteids of Cream.** By E. F. LADD (*J. Amer. Chem. Soc.*, 1898, 20, 858—860).—Casein was precipitated by adding a saturated solution of alum (3 c.c.) to 10 grams of cream diluted with water (80 c.c.); after 10 minutes, the solution was filtered, and the precipitate washed with water. The albumin was next separated by heating the filtrate to boiling, and filtering after a few minutes. The filtrate from the albumin was evaporated to about 50—60 c.c., and the albumoses precipitated by saturating with zinc sulphate. After 10—12 hours, it was filtered, the precipitate well washed, and the nitrogen determined. The peptones were determined in the filtrate by evaporating to a small bulk, when a portion of the zinc salt separated, and then adding absolute alcohol to 80 per cent. of the volume; after 12 hours, it was collected, washed with alcohol, and the nitrogen determined. As a check, the total nitrogen of the cream was also determined.

The following percentage results, obtained with (1) fresh cream and (2) ripened cream, are given.

	N in casein.	N in albumin.	N in albumoses.	N in peptones.	Total.	N in cream.
1.	0·237	0·035	0·031	0·023	0·326	0·335
2.	0·249	0·027	0·033	0·032	0·341	0·344

The results show that the method adopted involves no great losses, and that there is no very marked change in the proteids of cream during ripening.

N. H. J. M.

### Analytical Chemistry.

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**Hydrogen Sulphide as a Reagent.** By CARL GRAEBE (*Ber.*, 1898, 31, 2981—2982).—In the author's laboratory, precipitations with hydrogen sulphide are always carried out in closed vessels; for this purpose, small bottles are employed, into which the gas is passed by a tube, an expansion on which is ground into the neck of the bottle thus preventing all escape of gas into the air. The vessel is not closed until the air above the liquid has become displaced by hydrogen sulphide. The precipitation is accelerated by shaking.

J. J. S.

[**Estimation of Hydrogen Peroxide.**] By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1897, [vii], 11, 217—222. See this vol., ii, 149).



**Estimation of Perchlorate in Chili Saltpetre.** By FR. FREYTAG (*Chem. Centr.*, 1898, i, 1203; from *Zeit. öffentl. Chem.*, 4, 321—323).—Ten grams of the sample is heated in a covered porcelain crucible until effervescence has nearly ceased, and the crust formed on the cover is removed and put back into the crucible, which is again heated for 10 minutes. The contents are then dissolved in water, the solution acidified with pure nitric acid, boiled for 10 minutes, and the total chlorine estimated by Volhard's process.

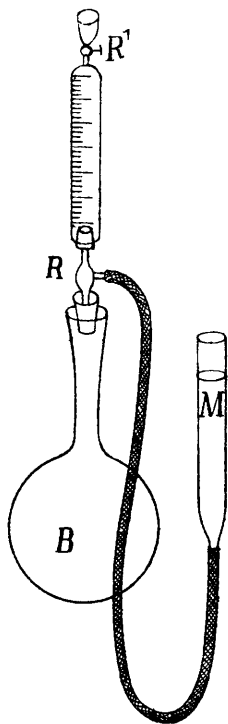
From this is deducted the chlorine present as chloride estimated in 10 grams of the sample by Volhard's process, and the difference is then calculated to potassium perchlorate. Allowance should be made for traces of iodate, if present.

L. DE K.

**Estimation of [Dissolved] Oxygen in Water.** By A. FLORENCE (*Chem. Centr.*, 1898, i, 474; from *Rép. Pharm.*, 1897, 385).—The round-bottomed flask B is filled with the sample of water and at once closed with a perforated indiarubber cork, fitted with a three-way stopcock, R. By means of the latter, B is connected at will with a graduated burette, furnished with a stopcock R', or, by means of an indiarubber tube, with the cylinder M, filled with mercury. By lifting M and opening R' the burette is filled with mercury. R' is then closed and M is lowered, which causes a vacuum in the burette. By turning R, the communication between the burette and M is intercepted, and established with B instead; the dissolved gas is now given off, and this may be accelerated by gentle warming. When no more gas is given off, the burette is again connected with M, the mercury in the two tubes is levelled, and the volume of gas is read off. After removing any carbonic anhydride by means of aqueous potash, the volume of oxygen is determined as usual by absorption with alkaline pyrogallol.

By means of this apparatus, estimations may be made in a very short time; this is very important, as the amount of dissolved oxygen may rapidly diminish owing to the action of bacteria.

L. DE K.



**Distinction between Ozone and Nitrous Acid or Hydrogen Peroxide.** By G. ERLWEIN and THEODOR WEYL (*Ber.*, 1898, 31, 3158—3159).—Ozone produces a wine-red coloration with a solution of metaphenylenediamine, both in presence of acids and alkalis. Since neither nitrous acid nor hydrogen peroxide produces any coloration with the diamine in presence of caustic soda, this reagent may be employed for distinguishing between ozone, on the one hand, and nitrous acid and hydrogen peroxide on the other. A freshly prepared solution of 0.1—0.2 gram of metaphenylenediamine

hydrochloride and 10 c.c. of 5 per cent. aqueous soda, made up to 100 c.c., is recommended as a suitable reagent, 25 c.c. of this giving a yellowish-brown coloration with 0.08 milligram of ozone in 5 seconds. Similar colours are produced with the corresponding ortho- and para-diamines. The authors propose to examine the atmosphere, and a number of animal and vegetable organs, and liquids, for ozone. A. H.

**Estimation of Sulphuric Acid.** By FÉLIX MARBOUTIN and ADRIEN PÉCOUL (*Bull. Soc. Chim.*, 1897, [iii], 17, 880—881).—The estimation of sulphuric acid as ammonium sulphate gives accurate results when the evaporation is carried out at 65°, but an increase of weight occurs when the residue is further heated on a water-bath at a temperature of 85—100°; above this temperature, the weight decreases again, and becomes normal at 120°. The authors regard this increase of weight as due to loss of ammonia and consequent absorption of water by the residual sulphuric acid; in support of this view, they show that the residue, after heating to 85°, has a marked acid reaction.

T. M. L.

NOTE.—According to Watson Smith (*Abstr.*, 1898, ii, 575), ammonium sulphate is dissociated, on heating, into the acid sulphate and ammonia, and not into sulphuric acid and ammonia.

T. M. L.

**Delicate Test for Ammonia and Nitrogenous Compounds which readily yield Ammonia.** By E. RIEGLER (*Chem. Centr.*, 1898, i, 272—273; from *Bull. Soc. Sci. Bucuresci*, 1897, 6, 335).—One gram of paranitraniline is dissolved in 20 c.c. of hot water and 2 c.c. of hydrochloric acid; 160 c.c. of water is added, the mixture well shaken, and when cold mixed with 20 c.c. of a 2.5 per cent. solution of sodium nitrite. Should the solution become turbid, it must be filtered.

Ten c.c. of the solution to be tested for ammonia, or compounds, like proteids, &c., which readily yield ammonia under the influence of strong alkalis, is mixed with 10—15 drops of the reagent and 10 per cent. aqueous soda is added drop by drop. In the presence of ammonia, reddish-yellow clouds appear, and, on shaking, the liquid turns yellow, or even red. If now excess of sulphuric acid is added, the colour vanishes, but on the surface of the liquid microscopic, yellow needles appear, which are soluble in alcohol, the solution giving an intense reddish-violet colour with aqueous soda.

L. DE K.

**Phosphorised Oil.** By H. EKROOS (*Arch. Pharm.*, 1898, 236, 627—635).—Both Dusart-Blondlot's method and the bromine method for the estimation of elementary phosphorus in phosphorised oil give results which are about 50 per cent. too low.

Phosphorised oil contains a portion of the dissolved phosphorus in the elementary condition, and a portion in the combined state, which is only slightly oxidised by bromine or nitric acid, is not volatile with steam, and of which the amount increases with the length of time the oil is kept. It seems probable that the phosphorus is combined with the fatty acids of the oil, but this could not be definitely proved.

A. W. C.

**Detection of Phosphorus in Insoluble Substances by Stereoelectrolysis.** By FRANÇOIS MAYENÇON (*Chem. Centr.*, 1898, i, 904; from *Rev. Techn.*, 1897, 398).—The process, which is applicable to phosphides and insoluble phosphates, is based on the liberation of phosphorus by the galvanic current, a sheet of platinum, zinc, or silver serving as anode. The substance is put on a piece of filter paper covering the anode, moistened with water or brine, and connected for a short time with the cathode; the liquid will then give the reactions for phosphoric acid. Or the substance may be moistened on a platinum foil with a few drops of molybdenum solution; the foil is then connected with the positive pole, and when the circuit is closed a yellow spot will make its appearance. L. DE K.

**Detection of Arsenic in Coal-Tar Colours.** By ALFRED ORTMANN (*Chem. Centr.*, 1898, i, 998—999; from *Zeit. Nahrungsm. Hyg. Waar.*, 12, 85—91).—Five grams of the dried colour is introduced into a tubulated retort, 5 c.c. of strong ferrous chloride added, and a current of pure hydrogen chloride is passed through the gently heated mixture; the vapours evolved are passed first through a Liebig's condenser, and then through a receiver containing water. After an hour's action, the distillate is introduced into the Marsh's apparatus, but should it contain sulphurous anhydride this is first oxidised by potassium chlorate and the excess of chlorine expelled by heating on the water-bath.

Or 5 grams of the sample is heated in a Kjeldahl flask with fuming nitric acid and evaporated to dryness; a mixture of 1 part of potassium sulphate and 2 parts of sulphuric acid is added, and the whole boiled until nearly colourless. When cold, the mass is dissolved in a little water, and then tested in the Marsh's apparatus. L. DE K.

**Volumetric Estimation of Boric Acid.** By H. COPAUX (*Compt. rend.*, 1898, 127, 756—759).—A known quantity of a soluble borate dissolved in a few c.c. of water is titrated with standard sulphuric or hydrochloric acid, using methyl-orange as indicator; the amount of acid required is a measure of the base combined with the boric acid; two volumes of an alcoholic solution of glycerol are now added, and the solution is titrated with N/4 caustic soda (free from carbonate) in the presence of phenolphthalein. The latter titration is repeated, under similar conditions, with a solution of pure boric acid and glycerol; the amount of boric acid in the soluble borate is determined from a comparison of the results. Solutions of soda and boric acid in ethylic alcohol may be employed, and the author applies the method to the estimation of boric acid in its alkyl salts; methylic alcohol, however, must be absent, as it interferes with the end-point. G. T. M.

**Estimation of Carbon in Cast Iron and Steel.** By HENRYK WDWISZEWSKI (*Zeit. anal. Chem.*, 1898, 37, 742).—The dissolution of iron in cuprammonium chloride and the subsequent dissolution of the precipitated copper are tedious operations if allowed to proceed in repose, but by vigorous skaking they can be greatly accelerated. The author employs a conical flask of 250—300 c.c. capacity, with a well

fitting stopper held down by a clip. In this is placed the weighed metal with 50 c.c. of copper solution for each gram of iron present, and the stoppered flask is immediately shaken in a shaking apparatus; the operation is complete in 5—8 minutes, and the carbon is obtained in a condition in which it can readily be collected and washed.

M. J. S.

**Estimation of the Alkaline Earths without previous Separation.** By JOHANNES KNOBLOCH (*Zeit. anal. Chem.*, 1898, 37, 733—740).—In consequence of the unsatisfactory character of all methods which depend on the complete separation of the three alkaline earths from one another, the author re-advocates the method of indirect estimation, and gives the preference to that form in which the mixed carbonates are weighed and then converted into oxides. This is effected by fusing the carbonates with borax which has first been heated to a constant weight in a platinum crucible (employing a Bunsen flame and a fire-clay crucible-jacket).

Putting  $p$  for the weight of the carbonates, and  $n$  for that of the oxides.

$2.00652915p - 2.58283141n$  = the CaO present when the other metal is barium.

$2.77369366p - 3.95263432n$  = the CaO present when the other metal is strontium.

$7.2546326p - 9.33816773n$  = the SrO present when the other metal is barium.

If the three metals occur together, the indirect method requires to be supplemented by the direct estimation of the barium; the solution containing the neutral chlorides of the three metals is divided into two portions, in one of which the barium is precipitated as chromate with the precautions laid down by Fresenius (*Abstr.*, 1891, 110, 500; 1893, 436); in the other, the three metals are thrown down as carbonates, and the values  $p$  and  $n$  (calculated on the total original solution) ascertained as above. Then putting  $r$  for the weight of the barium chromate (also in the total solution),

$\text{CaO} = 2.77369366p - 3.95263432n + 0.23080504r$ .

$\text{BaO} = 0.60367371r$ .

$\text{SrO} = n - \text{BaO} - \text{CaO}$ .

The test analyses communicated show that fairly close results are obtainable.

M. J. S.

**Detection of Cadmium in Presence of Copper by Adsorption.** By HEINRICH TREY (*Zeit. anal. Chem.*, 1898, 37, 743—747).—The author has devised a simple piece of apparatus, for the application of the principle first studied by Schönbein in 1861, that when a dilute solution containing several soluble substances is allowed to rise by capillarity in a piece of filter paper dipped into the liquid, the soluble substances are not only withdrawn by the paper from the water, but are arrested at different distances from the surface of the liquid. A narrow piece of glass-tube has one end widened into a funnel, and the other drawn out to a capillary point; the tube is then bent into a U form, and fixed with its open ends upwards. The solution can then be introduced by the funnel, and when it reaches the capillary point a disc of filter paper can be brought in contact

with the point, by resting it on a light wire frame, and allowed to remain until it has absorbed enough of the solution to form a wetted spot of any desired diameter. Solutions containing copper and cadmium are treated with excess of ammonia, and then diluted until the blue colour is scarcely visible. One of Schleicher's ash-free filters is allowed to absorb enough of the solution to wet the paper to a distance of 2.5 cm. from the capillary tube, and is then exposed to the vapour of ammonium sulphide, when the central black spot will be surrounded by a yellow ring of cadmium sulphide, the width and intensity of which will depend on the amount of cadmium present.

M. J. S.

**Detection and Estimation of Lead in Tin-plate and Tinned Foods.** By P. CARLES (*Chem. Centr.*, 1898, i, 798; from *Bull. Soc. Pharm. Bordeaux*).—For the estimation of lead in tin-plate, Riche's method is recommended, in which the lead is obtained as dioxide by electrolysis; this process is not interfered with by the presence of copper, but is rendered irregular by the presence of 5 per cent. of iron, and should more than 10 per cent. be present, the solution retains ferric stannate.

To detect lead in foods, these are burnt in a muffle, the charred mass is powdered and extracted with water to remove chlorides and alkali phosphates, and then burnt, with addition of sulphuric acid. The ash is treated with a mixture of 6 c.c. of nitric acid and 30 c.c. of sulphuric acid in 264 c.c. of water, and the solution submitted to electrolysis.

L. DE K.

**Volumetric Estimation of Mercury by Sodium Arsenite.** By C. REICHARD (*Zeit. anal. Chem.*, 1898, 37, 749—751).—The oxides of mercury are reduced to metal when heated with an excess of solution of sodium arsenite in excess of sodium hydroxide, with conversion of a corresponding amount of arsenite into arsenate; the un-reduced arsenite is then titrated by iodine or permanganate, after filtering hot and washing. The method seems capable of some degree of accuracy.

M. J. S.

**Alkalimetric Estimation of Metals. Estimation of Mercury.** By HENRI LESCŒUR (*Bull. Soc. Chim.*, 1897, [iii], 17, 706—712. Compare *Abstr.*, 1898, ii, 455).—Mercuric chloride may be estimated by titration with N/10 alkali, phenolphthalein being used as an indicator; it is necessary that the precipitated mercuric oxide should be separated by filtration, in order to minimise the disturbing influence of the mercuric oxide on the dissolved potassium chloride, a condition which is also attained by employing an alkali of N/100 strength. The use of helianthin leads to unsatisfactory results in this particular instance.

In the cases of mercuric sulphate and nitrate, which are only soluble in presence of excess of acid, the estimation of the metal may be accomplished by making two distinct titrations of the solution, one with helianthin in presence of common salt, which gives the amount of free acid, and the second with phenolphthalein alone, which gives the sum of the free acid and that of the mercuric salt itself.

Mercurous chloride, when boiled with alkalis, is decomposed in accordance with the equation  $\text{Hg}_2\text{Cl}_2 + 2\text{KOH} = \text{Hg} + \text{HgO} + 2\text{KCl} + \text{H}_2\text{O}$ , a reaction which may be taken advantage of in estimating mercurous salts. The authors recommend the same method for estimating chlorides in certain liquids, mercurous nitrate being used to precipitate the halogen as calomel. For practical details, the original paper must be consulted.

A. L.

**Volumetric Estimation of Osmium Tetroxide.** By EDUARD A. KLOBBIE (*Chem. Centr.*, 1898, ii, 65—66; from *Kon. Akad. Wetensch. Amsterdam*).—Osmium tetroxide may be estimated to 0.01 per cent. by treating its solution in dilute sulphuric acid with potassium iodide solution and titrating the liberated iodine with sodium thiosulphate; four atoms of iodine are liberated by each molecule of osmium tetroxide, osmium dioxide, potassium sulphate, and water being formed. The solution becomes dark green, and, even after remaining for days, no further reduction takes place; osmium dioxide is feebly basic, and probably the green coloration is due to the intermingling of the blue solution of this oxide in sulphuric acid with the solution of iodine.

E. W. W.

**Estimation of Organic Matter in Water by Potassium Permanganate.** By FÉLIX MARBOUTIN and MICHEL FRANCK (*Bull. Soc. Chim.*, 1897, [iii], 17, 888—890).—The authors show that Lévy's method in use in France gives results twice, or even thrice, as great as those obtained by the modified Forchammer method used in England; the French standard, however, allows twice as much organic matter, and the classification of the waters is consequently the same in both countries.

T. M. L.

**Assay of Iodoform.** By G. MEILLÈRE (*Chem. Centr.*, 1898, ii, 140; from *Anal. Chim. Anal. Appl.*, 3, 153—154).—One gram of the sample is introduced into a flask, or if a solution has to be tested, a suitable quantity is evaporated to dryness in the flask; to this, 25 c.c. of pure nitric acid is added and then 1.7 gram of silver nitrate. The flask, connected with a Liebig's bulb apparatus containing a little silver solution to serve as a trap, is now heated, gently at first, but more strongly towards the end; when no more nitrous fumes are evolved, the liquid in the flask is diluted to 150 c.c. and heated until quite clear. If the liquid in the bulbs is turbid, it must be added to the main bulk of liquid. The silver iodide is collected on a weighed filter, dried at 100°, and weighed.

L. DE K.

**Analysis of Aqueous Alcohol.** By CHESTER B. CURTIS (*J. Physical Chem.*, 1898, 2, 371—375).—If a definite quantity of aqueous alcohol is taken, the amount of toluene that must be added in order to produce a cloudiness increases as the amount of water in the alcohol decreases. The percentage purity of alcohols containing water may, therefore, be determined by titration with toluene. The method of operating suggested by the author for determining the percentage of alcohol (above 85 per cent.) in a mixture containing water, is to pipette off 10 c.c. of the solution, dilute with 1 c.c. water, and add toluene until the mixture clouds and clears at 0°. The following

table gives the number of c.c. of toluene required for alcohols differing by one-half per cent. from 85 to 100.

Per cent. alcohol.	c.c. toluene.	Per cent. alcohol.	c.c. toluene.	Per cent. alcohol.	c.c. toluene.	Per cent. alcohol.	c.c. toluene.
85.0	3.40	89.0	4.70	93.0	7.50	97.0	15.75
85.5	3.49	89.5	4.95	93.5	8.10	97.5	17.45
86.0	3.58	90.0	5.20	94.0	8.70	98.0	19.40
86.5	3.70	90.5	5.40	94.5	9.55	98.5	21.50
87.0	3.90	91.0	5.80	95.0	10.60	99.0	23.70
87.5	4.05	91.5	6.15	95.5	11.70	99.5	25.85
88.0	4.25	92.0	6.55	96.0	12.90	100.0	28.00
88.5	4.48	92.5	7.00	96.5	14.25		

It is obvious that the accuracy of the method is greater as the purity of the alcohol increases.

H. C.

**Detection of Glucose in Urine by Means of Methylene-Blue.** By ALFRED FRÖHLICH (*Chem. Centr.*, 1898, ii, 66—67; from *Centr. inn. Med.*, 1898, No. 4).—Ten c.c. of the urine is first freed from reducing colouring matters by mixing it with 5 c.c. of solution of lead acetate (3—10), and, then, after shaking, with 5 c.c. of basic lead acetate. The filtrate which, if not colourless, should be diluted with an equal bulk of water and treated with a little more solid lead acetate, is then tested for sugar as follows: 5 c.c. is mixed with 5 c.c. of a solution of methylene-blue (1:300) and 1 c.c. of 10 per cent. aqueous potash and boiled. If the colour of the mixture fades, sugar is present. As little as 0.04 per cent. may thus be detected.

L. DE K.

**Estimation of Sugar in Urine.** By W. SCHLOSSER (*Chem. Centr.*, 1898, i, 1209—1210; from *Pharm. Centr.-Halle*, 39, 259—261).—One hundred c.c. of the sample of urine is fermented with 4 grams of yeast in a long-necked flask closed with cotton wool, the fermentation being started by placing the flask in water of 35—40°; the whole is then kept for 12 hours at a temperature of 20°. After making sure that all the sugar has disappeared, the yeast is allowed to subside, the liquid poured off, the carbonic anhydride removed by agitating the liquid, and the sp. gr. is then carefully taken ( $D^1$ ). Another 100 c.c. of the sample is mixed with 2 c.c. of a 1.6 per cent. solution of salt, which the author calculates will introduce the same error in sp. gr. as the amount of added yeast does, and the sp. gr. is taken ( $D^2$ ). The difference  $D^1 - D^2$  is then multiplied by  $(V_2 : V_1) \cdot 229$  or  $(102:100) \cdot 229 = 233$ , in which formulæ  $V_1$  and  $V_2$  represent the respective volumes of the samples, and 229 the factor proposed by Roberts for calculating the amount of sugar from the loss in sp. gr.

If  $D^1$  and  $D^2$  are taken at different temperatures, a correction must be made. If  $t^1$  is the temperature of the urine and salt,  $t^2$  the temperature after fermentation, the difference  $t^1 - t^2$  should be multiplied by 0.0002, and the product added to  $D^1 - D^2$  when the tempera

ture lies between  $15^{\circ}$  and  $20^{\circ}$ . For temperatures between  $20^{\circ}$  and  $25^{\circ}$ , the factor 0.0003 should be used.

L. DE K.

**Estimation of Diabetic Sugars by the Polarimeter, by the Reducing Power, and by Fermentation.** By FRÉDÉRIC LANDOLPH (*Compt. rend.*, 1898, 127, 765—767. Compare Abstr., 1897, ii, 512, and 1898, ii, 148).—The author's investigations on the reducing power, fermentation, and thermo-optical properties of diabetic sugars, and on the appearance of their solutions when viewed through the polaristrobometer render it possible to divide these sugars into three classes which may be useful in the diagnosis of various glycosuric and diabetic affections.

G. T. M.

**Estimation of Sugar in Meat and Urine.** By EDUARD POLENSKE (*Chem. Centr.*, 1898, i, 1071—1072; from *Arbb. Kais. Ges. A.*, 14, 149—152).—Two hundred grams of finely comminuted meat, after being soaked for half an hour in 600 c.c. of cold water containing a little acetic acid, is heated to boiling, and when cold the mass is pressed through flannel, and then extracted twice more. The sugar is estimated in the united extracts by means of Peska's ammoniacal copper solution. Treatment with lead acetate is not advisable, as this might cause loss of sugar; precipitation by means of alcohol also is inadvisable. The extract is first filtered through paper, animal charcoal is added, and the whole evaporated on the water-bath until about 250 c.c. is left; it is then filtered, the charcoal well washed, and the filtrate again concentrated to 250 c.c. To the liquid, ammonia is added in slight excess, the whole diluted to 300 c.c., and after 15 minutes filtered and neutralised with acetic acid. It is then colourless and well adapted for the titration; it must, however, be borne in mind that urine, and more particularly meat, contains small proportions of reducing substances which in the analysis count as sugar.

It is more difficult to prove the presence of cane sugar, as this becomes partly inverted, whilst some components of the meat extract also suffer inversion when treated with acids. The author has, however, found that this may be reduced to a minimum by using 5 drops of hydrochloric acid for 100 c.c. of liquid, and heating for half an hour only; the extractive compounds, such as glycogen, are then but little affected, whilst the sugar is completely inverted.

The author also recommends Peska's process for the testing of diabetic urine; this should be diluted so as to contain about 0.5 per cent. of sugar.

L. DE K.

**Polarisation of Honey.** By R. FRÜHLING (*Chem. Centr.*, 1898, ii, 305; from *Zeit. öffentl. Chem.*, 4, 410—412).—The author calls attention to the fact that solutions of honey, when freshly prepared in the cold, show a very abnormal polarisation, caused by birotation. After the lapse of 5—6 hours, the polarisation is normal.

The error caused by this birotation is sometimes very large, and may amount to as much as  $-14^{\circ}$ . The author found that the normal polarisation is at once restored by adding to the liquid about 0.1 per cent. of ammonia; basic lead acetate should not be added, but the liquid should be clarified by means of alumina cream. It is also



advisable to dissolve the honey first in a little boiling water, as a high temperature destroys birotation. L. DE K.

**Estimation of Sugar in Chocolate.** By R. WOY (*Chem. Centr.*, 1898, i, 861; from *Zeit. öffentl. Chem.*, 4, 224—226).—The process recommended by de Koningh (*Abstr.*, 1898, ii, 314) is accurate, but rather slow, when applied to chocolate, unless the sample is first deprived of its fat. The author now proposes the following process, based on Scheibler's principle of double dilution. A 100 and a 200 c.c. flask are taken; half the normal weight of powdered chocolate (13.024 grams) is introduced into each, moistened with alcohol, and treated with water at 50°; after thoroughly shaking to dissolve the sugar, 4 c.c. of basic lead acetate solution is added, and, when cold, the liquids are made up to the mark and again shaken. The filtrates are now polarised in the 200 mm. tube. If  $a$  represents the polarisation of the 100 c.c. liquid,  $b$  that of the 200 c.c. liquid, and  $x$  the volume of the insoluble matter, including the lead precipitate, then the sugar in the 100 c.c. flask is dissolved in  $100 - x$  and the other in  $200 - x$  c.c. of water. Then  $a(100 - x) = b(200 - x)$ . L. DE K.

**Analysis of Brewing Sugars.** By GEORGE H. MORRIS (*J. Fed. Inst. Brew.*, 1898, 4, 162—176).—It is pointed out that, both in commercial glucoses and invert sugars, there is a certain amount of unfermentable matter which reduces Fehling's solution and is optically active. In the method of analysis proposed by the author, a correction is applied for this, and the true percentages of the fermentable sugars (dextrose, levulose, and maltose) are obtained. Details of the analytical methods adopted are given, as well as tables of optical constants and cupric-reducing power. A. C. C.

**The Correction for Unfermentable Reducing Substances in Sugar Analysis.** By TOM A. GLENDINNING (*J. Fed. Inst. Brew.*, 1898, 4, 363—365).—The author points out that raw cane sugars usually contain unfermentable Fehling-reducing substances, and that this may account partly for the presence of these substances in commercial invert sugars. Analyses are given in which the percentage varies from 0.47 per cent. to 2.64 per cent. This unfermentable matter was slightly dextrorotatory, and had a cupric-reducing power of about 30. A. C. C.

**Malt. I. The Ready-formed Sugars of Malt, and the Action of Diastase on Barley Starch.** By ARTHUR R. LING (*J. Fed. Inst. Brew.*, 1898, 4, 187—202).—Attention is called to the fact that in the estimation of the ready-formed sugars of malt by the method proposed by Moritz and Morris, the results are vitiated by the diastatic action taking place during the process of extraction. Experiments are described, showing that diastase does act appreciably on ungelatinised barley starch in the cold, but that this action can be entirely arrested by the presence of 0.0073 per cent. of free hydrochloric acid. Owing to the decomposition of organic salts by hydrochloric acid, this reagent cannot be used in the extraction of the sugars from malt. Results of experiments are given, showing that there is no formation of maltose when a solution containing 0.0168 per cent. of potassium

hydroxide is used for the extraction, and it is suggested that this might well serve as the basis of a method for the estimation of the sugars existing ready-formed in malt. A. C. C.

**Exact Estimation of Total Carbohydrates in Acid Hydrolysed Starch Products.** By GEORGE W. ROLFE and W. A. FAXON (*J. Amer. Chem. Soc.*, 1897, 19, 698—703).—The authors have determined the exact amount of carbohydrate present in solutions of commercial glucose, the specific rotatory power of the samples employed varying from  $[\alpha]_{D_3^{86}} = 70.5^\circ$  to  $[\alpha]_{D_3^{86}} = 164^\circ$ . The solutions were evaporated, and the residues dried at  $100-120^\circ$  in a vacuum apparatus, which is a modification of that of Lobry de Bruyn and Van Leent (compare Brown, Morris and Millar, *Trans.*, 1897, 79). When the specific gravity factors (that is, the excess of the specific gravity of a solution containing 1 gram of dry matter in 100 c.c.) are plotted as ordinates against the specific rotatory powers as abscissæ, a straight line is obtained. The authors conclude that, for solutions of acid hydrolysed starch products of sp. gr. varying from 1.035 to 1.045 at  $15.5^\circ$ , the sp. gr. factor ( $\Sigma$ ) may be calculated by the equation

$$\Sigma = 0.004023 - 0.000001329 (195 - [\alpha]_{D_3^{86}}).$$

A. R. L.

**Testing Formaldehyde.** By CARL E. SMITH (*Chem. Centr.*, 1898, i, 798—799; from *Amer. J. Pharm.*, 70, 86—94).—The author proposes the following tests for the purity and identity of the "formalin U.S.P." It should contain 35—40 per cent. of formaldehyde, to be estimated by Legler's ammonia process; it should be colourless, transparent, neutral or very faintly acid, and have a pungent odour and caustic taste. The sp. gr. should be about 1.08, and it should be miscible in all proportions with water and alcohol. When heated with ammoniacal silver nitrate or Fehling's solution, a deposit of metallic silver or cuprous oxide is obtained. If 2 c.c. is heated with 2 c.c. of aqueous potash and 0.5 gram of resorcinol, a red colour is developed. If 5 c.c. of sulphuric acid, containing a little salicylic acid, is added to 2 drops of the sample, a permanent dark-red coloration is obtained. If 1 c.c. of the solution is mixed with 5 c.c. of ammonia and evaporated to dryness on the water-bath, a white, crystalline residue is left, which, when heated with dilute sulphuric acid, gives the original pungent odour. One c.c., mixed with 10 c.c. of iodine solution and a sufficiency of aqueous potash, should give no iodoform reaction, showing the absence of acetone. The sample should also be quite free from any mineral matters. L. DE K.

**Estimation of Formaldehyde.** By OSKAR BLANK and H. FINKENBEINER (*Ber.*, 1898, 31, 2979—2981).—Three grams of the formaldehyde solution, or 1 gram of "solid formaldehyde," is dissolved in 25 c.c. of 2N sodium hydroxide; if the formaldehyde solution is stronger than 45 per cent., then 30 c.c. of alkali is employed. The mixture is placed in a tall Erlenmeyer flask and 50 c.c. of pure hydrogen peroxide free from acid (2.5—3 per cent.) run in through a funnel during the course of three minutes; the funnel is then washed out with distilled water, and the excess of alkali in the

flask titrated with 2N sulphuric acid, using litmus as an indicator. If the aldehyde solution contains less than 30 per cent. of formaldehyde, the mixture must be allowed to remain 10 minutes after the hydrogen peroxide has been run in. The number of c.c. of alkali which have been used up in converting the aldehyde into sodium formate, when multiplied by two, gives the percentage of formaldehyde in the original solution.

The results agree with those obtained by other methods employed in commercial analysis, but give higher values (about 1.5 per cent.) than the ammonia method.

J. J. S.

**Volumetric Estimation of Acetaldehyde.** By XAVIER ROCQUES (*Compt. rend.*, 1898, 127, 524—526).—The author has modified the method described by Rieter (*Abstr.*, 1897, ii, 606). He finds that alcoholic solutions of sulphurous acids and sulphites are much more stable than aqueous solutions; that alcoholic solutions of alkali-hydrogen sulphites are most suitable for the estimation of aldehyde; that in dilute solutions at least 12 hours is required to ensure complete combination; and that unless the proportion of aldehyde is very small, the sulphite compound is not completely decomposed by potassium hydroxide.

The sulphite solution is prepared by dissolving 12.6 grams of anhydrous sodium sulphite in 400 c.c. of water, adding 100 c.c. of normal sulphuric acid, diluting to 1000 c.c. with alcohol of 96°, and filtering after 24 hours. Ten c.c. of the alcoholic solution of aldehyde to be examined is placed in a 100 c.c. flask, mixed with 50 c.c. of the sulphite solution and made up to 100 c.c. with alcohol of 50°. A second quantity of 50 c.c. of the sulphite solution is placed in a similar flask, and made up to 100 c.c. with the same alcohol. After at least 12 hours, 50 c.c. is withdrawn from each flask, and the sulphurous acid estimated by means of decinormal iodine solution; the difference is the quantity of sulphurous acid that is in combination with the aldehyde; 1 c.c. of N/10 iodine = 0.0022 gram of aldehyde.

If the liquid to be examined contains less than 1 per cent. of aldehyde, the sulphite solution must be diluted; for 0.5 per cent., it should be diluted with an equal volume of alcohol of 50°, and N/20 iodine should be used; for 0.1 per cent., the sulphite should be diluted with alcohol of 50° to 10 times its ordinary volume, and centinormal iodine solution should be used.

C. H. B.

**Volumetric Estimation of Acetaldehyde.** By XAVIER ROCQUES (*Compt. rend.*, 1898, 127, 764—765. Compare preceding abstract).—The action of alkali hydrogen sulphites on acetaldehyde, when carried out at 15°, is not complete after 48 hours. The solution to be examined should be mixed with a known volume of alcoholic bisulphite solution, made up to 100 c.c. with 50 per cent. alcohol in a stoppered flask, and heated for 4 hours at 50°; a blank experiment should also be performed in another flask containing similar quantities of bisulphite and alcohol, and at the end of the time both solutions should be titrated with iodine in the manner previously indicated.

G. T. M.

**Detection of Acetone in Urine.** By B. STUDER (*Chem. Centr.*, 1898, i, 1152; from *Schweiz. Woch. Pharm.*, 36, 149—151).—The author combines the methods proposed by Legal, and Lieben and Dragendorff; 50 c.c. of the sample of urine is mixed with 5 c.c. of dilute sulphuric acid and submitted to distillation, the distillate being collected in a test-tube placed in cold water. When 3 c.c. has passed over, 6 to 10 drops of a freshly-prepared 10 per cent. solution of sodium nitroprusside, and 1—2 drops of aqueous soda are added; if acetone is present, a purple-red coloration is produced. If the reaction is not decided enough, it may be advisable to add 6 to 8 drops of acetic acid, when a claret colour will prove the presence of acetone. The reaction is interfered with by hydrogen sulphide, which is occasionally present in stale urines. L. DE K.

**Soap Analysis.** By RUDOLF HEFELMANN and ERNST STEINER (*Chem. Centr.*, 1898, ii, 142—143; from *Zeit. öffentl. Chem.*, 4, 389—396).—The estimation of the fatty acids in soaps made from Ceylon oil is attended with some inaccuracies which are avoided by using the authors' process. The fatty acids and other fatty matters are liberated by a mineral acid, and extracted by ether; this solution is neutralised by N/2 potash, using phenolphthalein as indicator, and the whole is dried over a weighed quantity of sand at 100°. The amount of fatty acids and neutral fats may then be easily calculated.

Equally accurate results are obtained by evaporating the ether and drying the residue at 55°; at a higher temperature, some of the fatty acids volatilise. Light petroleum should not be used, as it does not dissolve the acids completely. L. DE K.

**Relation between the Sp. Gr. and the Insoluble Fatty Acids of Butter and other Fats.** By NORMAN LEONARD (*Analyst*, 1898, 23, 282—283).—It is well known that animal fats used for making butter substitutes have a much lower sp. gr. than butter-fat itself, and the author states that the relation between the sp. gr. at 100° F. and the percentage of insoluble fatty acids yielded by the sample may be approximately represented by the formula  $y = k(1 - x)$ , where  $y$  is the percentage of insoluble acids, and  $x$  the sp. gr. of the melted fat at 100° F., water at 60° F. being taken as unity.  $k$  is a constant which may be taken as = 951 on an average.

When the butter mixture contains animal fats, the percentage of fatty acids actually found will at the most differ by 1.4 per cent. from that calculated by the formula. But when vegetable oils such as cotton-seed oil, cocoa nut oil, or sesamé oil have been used, the formula will no longer agree. L. DE K.

**Chemistry of Drying Oils: Examination of Linseed Oil.** By OTTO HEHNER and CHARLES A. MITCHELL (*Analyst*, 1898, 23, 310—318).—The paper is chiefly devoted to a criticism of the work done by Hazura and Grüssner (*Abstr.*, 1888, 817; 1270). Their results are, on the whole, verified by the authors.

By dissolving 1—2 grams of linseed oil in 40 c.c. of ether and a few c.c. of glacial acetic acid, cooling the mixture in ice, and adding

bromine, a precipitate is obtained which may be collected, washed with cold ether, and finally dried in a water-oven until the weight becomes constant. The process seems a valuable one for the assay of commercial raw linseed oil, as the pure article yields from 24—25 per cent. of brominated deposit, whilst common adulterants such as cotton-seed oil either yield no deposit at all, or but a trifling quantity, as in the case of walnut oil, for instance. Marine animal oils, however, also yield abundant precipitates, and cannot be detected by the bromine test.

L. DE K.

**Estimation of Fat in Animal Tissues and Fluids.** By JOSEPH NERKING (*Pflüger's Archiv.*, 1898, 73, 172—183. Compare Abstr., 1898, 413).—This paper is a defence of the method introduced by Dormeyer, who subjects meat, &c., to gastric digestion before extracting it with ether. A new piece of apparatus for performing the extraction is described and figured. Hydrochloric acid has no deleterious action on fatty acids.

W. D. H.

**Analysis of Bone Fats.** By AL. A. SHUKOFF and P. J. SCHESTAKOFF (*Chem. Centr.*, 1898, i, 864—865; from *Chem. Rev. Fett. u. Harz-Ind.*, 5, 5—8).—Moisture is estimated by drying 5 grams of the sample in a current of air, or carbonic anhydride, at 100—110°. Foreign admixtures are found by treating the dried fat with light petroleum, which, however, also dissolves any lime soaps. The ash is obtained by burning the fat, and it is then tested for lime with standard acid. To make a direct estimation of the fatty matter, 10 grams of the sample is mixed with 3—5 drops of strong hydrochloric acid to decompose the lime soaps, and the fatty matter is extracted by means of light petroleum; any insoluble matter is collected on a weighed filter, which is then well washed and the bulk of the light petroleum being distilled off, the remainder is removed by drying the fat as before in a current of carbonic anhydride at 100—110°.

The unsaponifiable matter is estimated by evaporating 5 grams of the fatty matter to dryness with 25 c.c. of 8 per cent. alcoholic soda in a porcelain dish; the soap is dissolved in 80 c.c. of water, and three times extracted with 80 c.c. of ether; if the layers will not separate readily, this may be accelerated by adding a little alcohol. The ethereal solution is evaporated to dryness, and the residue treated with a little aqueous soda and then with light petroleum; the latter, on evaporation, leaves the unsaponifiable matter in a state of purity. The solidifying point is taken according to Dalican's directions.

L. DE K.

**Analysis of Fats: Preparation and Crystallisation of Cholesterol and Phytosterol.** By A. BÖMER (*Chem. Centr.*, 1898, i, 466—467; from *Zeit. Unters. Nahr. u. Genussm.*, 1898, 21—49).—The author proposes a modification of Salkowski's process. Fifty grams of the fat, melted in an Erlenmeyer flask fitted to a reflux condenser, is saponified with 100 c.c. of 20 per cent. alcoholic potash, the soap introduced into a separating funnel, 200 c.c. of water added, and the whole extracted by shaking with 500 c.c. of pure ether; after removing the ether, the extraction is twice repeated, using 250 c.c. of ether

each time. The ether is then distilled off from the mixed extracts, and the residue again saponified with 10 c.c. of the alcoholic potash; 20 c.c. of water is added, and the shaking repeated with 100 c.c. of ether. This, after being freed from traces of soap by washing thrice with 10 c.c. of water, is left to evaporate spontaneously; the residual cholesterol or phytosterol must then be recrystallised from boiling absolute alcohol.

It appears that the microscopical appearance of the two substances depends on various circumstances, but, as a rule, cholesterol forms thin, rhombic tablets, whilst phytosterol yields thin needles. In doubtful cases, the melting point should be taken. If both are present, a kind of mixed crystal is obtained, which looks either somewhat like cholesterol or phytosterol.

L. DE K.

**Analysis of Fats: Melting Points of Cholesterol and Phytosterol; Amount of Unsaponifiable Matter in Fats.** By A. BÖMER (*Chem. Centr.*, 1898, i, 638—639; from *Zeit. Unters. Nahr. u. Genusssm.*, 1898, 81—96).—The author estimated the amount of cholesterol in lard and butter-fat by his process (preceding abstract), and obtained, on an average, 0.1774 per cent. of crude cholesterol from lard and 0.3512 per cent. from butter. These figures are higher than those obtained by Salkowski. Cholesterol melts at 146—148°, whilst phytosterol melts at 135.5—141°. Mixtures of the two have a melting point varying but slightly from the calculated figure.

The phytosterol test enables the presence of commercial margarine in butter, or of cotton-seed oil in lard, to be detected with certainty if the chemical analysis of these articles leaves any doubt. It is, however, not so easy to detect small percentages of animal fats in vegetable oils.

L. DE K.

**Volumetric Estimation of Methylic Salicylate.** By EDWARD KREMERS and MARTHA M. JAMES (*Chem. Centr.*, 1898, i, 1070; from *Pharm. Rev.*, 16, 130—133).—The authors have slightly modified the method proposed by Ewing, and now boil a weighed quantity of the substance with a known volume of normal alkali for 5 minutes. The excess of alkali is then titrated with normal acid, and the alkali consumed, multiplied by 0.152, represents the number of grams of methylic salicylate.

The method proposed by Messinger and Vortmann is also recommended. Five grams of the sample is saponified with excess of alkali, and when cold diluted to 500 c.c.; 10 c.c. of this is heated, 50 c.c. of N/10 iodine solution added, and the liquid diluted to 500 c.c.; in 100 c.c. of this, the excess of iodine is estimated by means of N/10 sodium thiosulphate. One c.c. of iodine solution absorbed, when multiplied by 0.631825, represents the amount of methylic salicylate, as 1 mol. of the ethereal salt absorbs 7 mols. of iodine.

L. DE K.

**Detection of  $\alpha$ -Naphthol in  $\beta$ -Naphthol.** By A. DUBOSC (*Chem. Centr.*, 1898, i, 800; from *Bull. Soc. Ind. Rouen*, 1897, 434).—If a solution of  $\alpha$ -naphthol is mixed with a few drops of sodium hypobromite solution (30 c.c. aqueous soda of sp. gr. = 1.33, 100 c.c. of water, and 5 c.c. of bromine), a dirty violet coloration is produced, but  $\beta$ -naphthol

only gives a pale yellow colour. The author now proposes to use this reaction for testing commercial samples of  $\beta$ -naphthol which, should they contain even as little as 3 per cent. of the  $\alpha$ -compound, are useless for preparing dyes.

L. DE K.

**Examination of Camphor Liniment.** By NORMAN LEONARD and H. METCALFE SMITH (*Analyst*, 23, 281—282).—This drug being often deficient in camphor, the authors ascertain the amount present by drying 3 or 5 grams of the sample for 2 hours at  $120^{\circ}$  in a flat-bottomed dish. The loss, after adding 0.15 per cent. to compensate for the gain in weight caused by the oxidation of the olive oil, should amount to 21.45 per cent.

Assuming the sp. gr. of the olive oil to have been 0.9164, the amount of camphor may be calculated from the sp. gr. of the sample, each per cent. of camphor raising the density by 0.00045. Mineral oil is sometimes employed instead of olive oil, but this fraud is readily detected by the insolubility of the sample in hot alcoholic potash.

L. DE K.

**Action of Iodine on Antipyrine. Estimation of Antipyrine or of Iodine.** By J. BOUGAULT (*Chem. Centr.*, 1898, i, 858; from *J. Pharm.*, [vi], 7, 161—163).—The author has found that 1 mol. of antipyrine dissolved in alcohol containing mercuric chloride absorbs exactly 1 mol. of iodine; or 1 gram of antipyrine = 1.351 grams of iodine.

To estimate antipyrine, 20 c.c. of a 1 per cent. alcoholic solution is mixed with 20 c.c. of a 2.5 per cent. alcoholic solution of mercuric chloride and an alcoholic solution of iodine containing 1.351 grams of iodine in 100 c.c. of 95 per cent. alcohol is added until a permanent, yellowish coloration is noticed. If the antipyrine is pure, it will consume exactly 20 c.c. of iodine solution; if not, it will take proportionally less. An iodine solution may, in turn, be estimated by means of a standard solution of antipyrine.

L. DE K.

**Reactions of Alkaloids with Benzaldehyde and Sulphuric Acid.** By HERM. MELZER (*Zeit. anal. Chem.*, 1898, 37, 747—748).—Besides picrotoxin (*Abstr.*, 1898, ii, 651), only a few other alkaloids and poisons produce colours with benzaldehyde and sulphuric acid. It is best to use a 20 per cent. solution of benzaldehyde in absolute alcohol, a drop of this solution being added to a trace of the alkaloid in a watch-glass, and then a single drop of concentrated sulphuric acid without any stirring. Digitalin gives brown streaks; veratrine, a red coloration; codeine, a yellow to blood-red; thebaine, a dark brown; delphinine, reddish-brown streaks; morphine, red to yellowish-red streaks; whilst colchicine, cantharidin, coniine, nicotine, brucine, strychnine, aconitine, papaverine, narcotine, hyoscyamine, emetine, apomorphine, and narceine give no characteristic colours.

M. J. S.

**Estimation of Nicotine in Tobacco.** By C. C. KELLER (*Chem. Centr.*, 1898, ii, 388—389; from *Ber. Deutsch. Pharm. Ges.*, 8, 145—152).—The author recommends the following process: 6 grams of tobacco dried over quicklime is powdered and treated in a stoppered bottle with 60 grams of ether, 60 grams of light petroleum,

and 10 c.c. of 20 per cent. aqueous potash; the mixture is well shaken for half an hour, then left for 3 or 4 hours, and 100 grams of the ethereal liquid is collected in a 200 c.c. bottle; after a strong current of air has been passed through to expel any ammonia present, 10 c.c. of alcohol, one drop of a 10 per cent. solution of iodeosin, and 10 c.c. of water are added, and the whole is well shaken, which causes the iodeosin and the nicotine to pass into the aqueous liquid. N/10 hydrochloric acid is now added until the liquid is colourless, and the slight excess of acid is titrated by means of N/10 ammonia. One c.c. of acid = 0.0162 gram of nicotine.

Analyses are given showing the amount of nicotine in various brands of tobacco and cigars, from which it appears that so-called strong tobaccos do not necessarily contain a high percentage of nicotine.

L. DE K.

**Estimation of Morphine in Opium.** By HERMANN THOMS (*Chem. Centr.*, 1898, ii, 136; from *Ber. Deutsch. Pharm. Gesell.*, 8, 124—125).—The author condemns the so-called brine method proposed by Montemartini and Trasciatti for the assay of opium (*Abstr.*, 1898, ii, 270) as being too tedious, and giving results which are too low.

L. DE K.

**Action of Sulphuric Acid on Strychnine when separating this Alkaloid from Organic Matters.** By EDGAR H. S. BAILEY and WM. LANGE (*Chem. Centr.*, 1898, i, 478; from *Amer. J. Pharm.*, 70, 18—21).—The authors find that the treatment with sulphuric acid so modifies the strychnine that it requires more than four times the usual amount to get a satisfactory reaction with the potassium dichromate test. Matters are even worse, if, after the acid treatment, the alkaloid is extracted by means of aqueous potash and chloroform. Minute traces of the alkaloid may, therefore, escape detection altogether.

L. DE K.

**Estimation of Indigo: Brandt's Method.** By ALBERT BRYLINSKI (*Chem. Centr.*, 1898, i, 1041; from *Bull. Soc. Ind. Mulhouse*, 1898, 33—39).—The extraction of indigotin by means of boiling aniline is attended by two serious sources of error; if the extraction is continued for 3—4 hours, about 30—40 per cent. of the indigo may be decomposed; on the other hand, the indigotin crystals retain about 10 per cent. of aniline. As, however, in Brandt's process the boiling only lasts for half an hour, the two errors fairly well compensate one another, so that the result is technically accurate.

The acetic acid process gives almost theoretically correct results. The sample is extracted in a Soxhlet's apparatus with boiling glacial acetic acid until the acid runs off colourless; on diluting the extract with four times its bulk of water, the indigotin is completely precipitated and may be collected on a weighed filter. It is washed first with hot water, and then with alcohol and ether to free it from certain impurities extracted from the paper filter by the strong acid.

L. DE K.

**Heller's Test for Detecting Blood in Urine.** By V. ARNOLD (*Chem. Centr.*, 1898, i, 1002; from *Rev. Klin. Wochschr.*, 35, 283—285).—This well-known test is based on the fact that aqueous



potash, on warming, precipitates the earthy phosphates from urine, which, in the presence of blood, assume a ruby-red colour; the test does not depend on the formation of hæmatin, but of hæmochromogen. As, however, the reaction may be also due to the presence of melanin or urobilin, the author advises not to trust to Heller's test alone, but always to confirm the result by means of the spectroscope. Blood spots may be dissolved in aqueous potash, and urine may then be added; the addition of ammonium sulphide becomes superfluous.

L. DE K.

**Guaiacol Test for Blood.** By EDUARD SCHAER (*Arch. Pharm.*, 1898, 236, 571—579).—The author finds that a 65—80 per cent. solution of chloral hydrate is an excellent solvent for blood, and proposes to modify the guaiacol test in the following manner.

The blood stain, after moistening with glacial acetic acid, is treated with a concentrated solution of chloral hydrate. To a small portion of the extract, guaiacol is then added, and either hydrogen peroxide or Hünefeld's reagent, when the blue colour is produced with remarkable delicacy.

A. W. C.

**Simplified Test for Peptone in Urine.** By ERNST FREUND (*Chem. Centr.*, 1898, i, 637; from *Wien. Klin. Rundsch.*, 1898, 37).—The urine is freed from nucleo-albumins, albumin, and protalbumoses by means of a 10 per cent. solution of lead acetate, two drops being generally sufficient for 10 c.c. of urine. Should, however, the urine contain from 0.1 to 3 per cent. of albumin, this must be first removed by coagulation with a few drops of dilute acetic acid at the boiling heat. The filtrate is then carefully neutralised with soda before adding the lead solution. The second filtrate, which should not give any reaction with acetic acid and potassium ferrocyanide, showing absence of excess of lead, is now used for the biuret test. One part of peptone may thus be detected in 12,000 parts of urine.

L. DE K.

**Precipitation of Albumoses by Zinc Sulphate.** By K. BAUMANN and A. BÖMER (*Chem. Centr.*, 1898, i, 640; from *Zeit. Unters. Nahr. u. Genussm.*, 1898, 102—126).—The authors state that zinc sulphate may be advantageously used instead of the ammonium salt in the analysis of meat extracts, &c. The solution, which must be free from coagulable albumin and contain about 1 gram of solid matter in 50 c.c., is acidified with 1 c.c. of dilute sulphuric acid (1 : 4) and gradually saturated with zinc sulphate, using very finely-powdered salt towards the finish. The liquid is filtered after being kept overnight, and the precipitate washed with a slightly acidified saturated solution of zinc sulphate. The amount of albumose is then found by treating the precipitate by Kjeldahl's process. In the filtrate, the peptones, meat-bases, and ammonia are precipitated by the ordinary solution of phosphotungstic acid to which half its volume of dilute sulphuric acid (1 : 8) has been previously added.

After being first kept for some time at 60—65°, the mixture is allowed to remain for 24 hours in a cool place; it is then filtered, and the precipitate, after being washed with dilute sulphuric acid (1 : 6), is treated by Kjeldahl's process.

Ammonia may be estimated in a second phosphotungstic precipitate by distillation with magnesia, and must be allowed for when calculating the amount of peptones and meat-bases from the result of the nitrogen estimation.

L. DE K.

**Detection of Dextrin, Gelatin, and Gum in Desiccated Albumin.** By A. A. BONNEMA (*Chem. Centr.*, 1898, ii, 386; from *Pharm Centr.-Halle*, 39, 424—425).—Ten grams of the powdered white of egg is well stirred with water, boiled to coagulate the albumin, and after a few minutes the liquid is filtered and a portion of the filtrate put aside to cool at a low temperature for 24 hours; if it turns to a jelly, gelatin is present. Another portion is mixed with alcohol in excess, and if a permanent precipitate is obtained, gelatin, dextrin, or gum is present; the former precipitate disappears on adding a little nitric acid. Dextrin may be identified in the filtrate by the red coloration produced with iodine, and gum by the precipitate given with basic lead acetate. Dieterich's iodine absorption test for the purity of albumin is not recommended by the author.

L. DE K.

**Estimation of Gelatin in Gums and Food Materials.** By AUGUSTE TRILLAT (*Compt. rend.*, 1898, 127, 724—725).—In estimating the amount of gelatin present in a sample of gum arabic, the substance is dissolved in water, filtered if necessary, evaporated to a syrupy consistency, treated with excess of formaldehyde solution, and the evaporation continued until the mixture becomes pasty; it is then extracted with water to remove the gum and the gelatin rendered insoluble by the aldehyde, is dried at 100° and weighed. The results obtained agree to 1 per cent., and the method serves to distinguish between artificial jellies containing gelatin and those derived from vegetable sources. The increase in weight of the gelatin due to the fixation of formaldehyde is inappreciable, owing to the great difference between their molecular weights. If the sample to be analysed contains proteid substances coagulated by heat, these are first removed by warming the solution; the filtrate should be concentrated before the addition of formaldehyde, as no precipitate is produced in dilute solutions.

G. T. M.

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## General and Physical Chemistry.

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**Relation between Luminous Energy and Chemical Energy : The Reciprocal Displacement of Oxygen and the Halogens.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1898, 127, 795—798).—The author has stated (this vol., ii, 1) that both iodic acid and iodic anhydride are slowly decomposed at the ordinary temperature, either by heat or by direct sunlight, into iodine and oxygen ; it is now shown that this action is non-reversible, no change appearing to take place when oxygen in contact with iodine, either dry or in presence of water, is left exposed in a sealed tube during 5 months to bright sunshine. Direct combination between iodine and oxygen is impossible, because such a change would be endothermic. Bromine and chlorine do not combine directly with oxygen, but, on the other hand, decompose water with liberation of oxygen ; in the case of bromine, the action is hardly perceptible in darkness, but is much more apparent in sunlight. The reaction is, however, reversible, cold concentrated hydrobromic acid being decomposed by oxygen under the influence of sunlight (*Abstr.*, 1890, 6) ; with dilute hydrobromic acid, however, a similar action occurs only very slowly, if at all. Pure concentrated hydrochloric acid is not acted on by oxygen ; if, however, a trace of a metal such as manganese or iron is present, decomposition takes place, chlorine being evolved (*loc. cit.*). W. A. D.

**Spectra of Compounds.** By ARNAUD DE GRAMONT (*Bull. Soc. Chim.*, 1897, [iii], 17, 774—778).—In view of the confusion which frequently arises in the discussion of the spectra of compounds, the author emphasises the distinction between *line-spectra*, or *atomic spectra*, due to the elements themselves and probably to the atoms thereof, and *band-spectra*, which are produced by undecomposed compounds, and may, therefore, be termed *molecular spectra*. The spectra consisting of fluted bands, capable of resolution into groups of lines, form a third class, which is not further considered here. Under the ordinary laboratory conditions, when a solution or a fused salt is heated by a Bunsen flame or an electric spark, a mixed spectrum is observed, consisting of the principal lines due to the metal, and of bands belonging either to the salt itself, or to simpler compounds, such as metallic oxides, produced by its decomposition.

To the first class of spectra above mentioned belong dissociation spectra, obtained by means of a condensed electric spark, and consisting of all the lines characteristic of the elements contained in the compound examined. The principal lines, owing to the condensation, are rendered diffuse, so as to have the appearance of bands ; this is more especially the case with the non-metallic elements and with the more refrangible rays. A highly condensed spark is, however, favourable to the appearance of the more feeble lines. Dissociation spectra, whether obtained with a solid compound or with a fused salt, exhibit

essentially the same characters, except that, in the latter case, the atmospheric lines are almost completely absent from the spectrum.

The successive appearance and disappearance, in a constant order, of various lines in an elementary spectrum is to be observed both when the same substance is subjected to electric discharges of varying intensity, and also when, under constant electrical conditions, the proportion of an element in the substance examined increases from zero to an amount giving all the lines characteristic of the element. Valuable conclusions may be drawn from the duration of the lines belonging to an element which forms but a very small proportion of the substance examined; the time of visibility appears to be a function of, if not proportional to, the amount of the element volatilised. The intermittent or irregular appearance of certain lines may afford indications of the structure of the substance, if this is a solid, or of the distribution of the elements therein. The presence of a small proportion of an element in a substance may be manifested by a spectrum which is (1) persistent, consisting of the principal lines, (2) transient, or (3) intermittent and irregular. It should be noted that the delicacy of spectral reactions varies with different elements. N. L.

**Dissociation Spectra of Fused Salts. Alkali Metals: Sodium, Lithium, Potassium.** By ARNAUD DE GRAMONT (*Bull. Soc. Chim.*, 1897, [iii], 17, 778—780, 780—782).—The lines characteristic of the metals sodium, potassium, and lithium were obtained by deducting from the complete spectrum of various dissociated salts the lines due to the non-metallic elements, and also by observation of the spectrum of the carbonates under special conditions.

*Sodium*.—6161 and 6155, strong and bright; 5896 and 5890, intense; 5688 and 5683, strong and bright; 5675 and 5670, feeble; 5155 and 5151, fairly strong; 4983 and 4979, very distinct, very diffuse, and nearly confused; \*4572, feeble and diffuse; \*4670, fairly distinct but diffuse; \*4545, feeble and diffuse; \*4499, fairly distinct but diffuse.

Owing to the condensation, the doublets marked with an asterisk appear as diffuse bands.

*Lithium*.—6708, strong and bright; 6103, very strong; 4972, strong; 4603, strong, large, and diffuse; 4273, very distinct; 4132, very distinct and very diffuse.

*Potassium*.—7699 and 7666, visible with difficulty; 6939, fairly strong; 6911, very well marked; 6308, well marked; 6245·5, very distinct; 6117·5, very well marked; 5832, strong; 5811, very fairly distinct; 5801, strong; 5783, very well marked; 5515, feeble; 5360, very distinct and diffuse; 5344, very fairly distinct and diffuse; 5340, very distinct and diffuse; 5323·5, very fairly distinct and diffuse; 5113 and 5099, very fairly distinct, diffuse, and nearly confused; 5051 and 5007, feeble; 4855·5 and 4851, very fairly distinct; 4829, fairly strong; 4652 and 4606, very fairly distinct; 4506·5 and 4466, feeble; 4388 and 4309·5, very fairly distinct; 4306·5, very fairly distinct; 4264, fairly strong; 4225·5 and 4222·5, very fairly distinct; 4210, feeble; 4185·5, fairly strong and broad; 4045·5, strong, very broad, and diffuse. N. L.

**Spectra of Aluminium, Tellurium, and Selenium.** By ARNAUD DE GRAMONT (*Compt. rend.*, 1898, 127, 866—868).—The lines at  $\lambda = 6371\cdot3$ ,  $6344\cdot8$ , and  $5056\cdot6$ , observed by Thalén in the spectrum of aluminium, are not visible when the metal employed has been carefully purified. The first two coincide in position with the very strong lines,  $6369\cdot7$  and  $6342\cdot2$ , of the doublet  $\text{Si}\alpha$ , observed by the author in the spark spectrum of silicon (*Abstr.*, 1897, ii, 238; the line  $6369\cdot7$  was, by a misprint in the original paper, given as  $6969\cdot7$ ). The third line probably corresponds with the line  $5060\cdot0$  of the strongly defined doublet  $\text{Si}\gamma$ , the second line of which was not recorded by Thalén owing to its nearly coinciding with the line  $5045\cdot1$  of the spectrum of air. The line  $4445\cdot2$ , observed in the spectrum of aluminium by Hartley and Adeney (*Phil. Trans.*, 1884, 101), is probably identical with the line  $4445\cdot8$  of air.

The green lines,  $5217$ ,  $5153$ , and  $5105$ , in the spectrum of tellurium (Thalén) are probably due to copper, as they are visible neither in spectra of tellurites or tellurates, nor in that of tellurium from which all traces of copper and antimony have been removed; Demarçay, also, has failed to observe their presence in the case of a solution of tellurium in hydrochloric or hydrofluoric acid. The same copper lines are present in Plücker and Hittorf's spectrum of selenium, and the author himself has previously noted their presence in the same spectrum (*Abstr.*, 1895, ii, 338); he now finds, however, that in his own case they were due to the platinum he employed to furnish the spark being contaminated with copper. The lines cannot be observed in the spectra of pure selenates or selenites, although they are invariably present in the spectra of seleniferous minerals, notably in the case of clausthalite ( $\text{PbSe}$ ).

W. A. D.

**Rotatory Dispersion of Tartaric Acid and Turpentine Oil.** By GEORGE V. WENDELL (*Ann. phys. Chem.*, 1898, [ii], 66, 1149—1161).—The rotation of tartaric acid solutions was measured for the Fraunhofer lines  $C$ ,  $D$ ,  $E$ ,  $b$ , and  $F$ . With increasing concentration, the maximum is displaced towards the red end of the spectrum, so that with a 50 per cent. solution it is found in the green. The specific rotation decreases with increasing concentration, but the rate of decrease is very different in different parts of the spectrum, being lowest in the red; on the other hand, the specific rotation increases rapidly with rising temperature, the rate of increase being greater for the concentrated than for the dilute solutions. The effect of rising temperature is to displace the maximum rotation towards the violet end of the spectrum.

Measurements with dextro- and lævo-turpentine oil show a perfect regularity in the behaviour of these substances, as the rotation increases with the refrangibility of the rays used. Mixtures of the two oils were also examined, and it was found that the observed rotations differ slightly, but quite definitely, from those calculated with Biot's formula for mixtures of optically active compounds.

H. C.

**Thermochemical Theory of the Carbon Cell.** By DONATO TOMMASI (*Bull. Soc. Chim.*, 1897, [iii], 17, 963—964).—The author has previously described an electric element in which the electrodes

are of carbon, one being coated with lead peroxide, and immersed in a solution of sodium chloride (Abstr., 1887, 756), and he regarded the action as due to the oxidation of the uncoated carbon and the reduction of the peroxide. Reed (*Electrical Review*, 1896) considered the current to be due to the action of the sodium chloride on the lead peroxide, but this view is untenable, as in that case the coated carbon should be the negative electrode, whereas the reverse obtains. Further, the E.M.F., calculated according to the author's view of the action, is equal to that actually found for the element. L. M. J.

**Dissolving of Platinum and Gold in Electrolytes.** By MAX MARGUELES (*Ann. Phys. Chem.*, 1898, [ii], 66, 540—543).—The author makes some additions to his former statements (Abstr., 1898, ii, 497) with reference to the dissolving of platinum and gold in electrolytes. The dissolution of platinum takes place only at the anode when the cation of the electrolyte is hydrogen; in salt solutions, the platinum is attacked simultaneously at both anode and cathode. Platinum not only dissolves in the electrolytes previously named, but also in phosphoric, formic, and acetic acids; oxalic acid is, however, without effect. H. C.

**Ammonium Amalgam.** By POCKLINGTON (*Chem. Centr.*, 1898, ii, 853; from *Elektrician*, 41, 457).—In order to prepare ammonium amalgam and to measure the E.M.F. between a mixture of the amalgam with mercury and a strip of copper immersed in copper sulphate solution, the author uses a cell containing mercury and divided into two portions by a partition which dips into the mercury, but does not reach to the bottom of the cell. The ammonium amalgam, prepared by electrolysis of a solution of ammonium chloride in one half of the cell, quickly diffuses into the mercury in the other half, and here the E.M.F. between the mixture and a copper electrode in a solution of copper sulphate is tested. Whilst, before the passage of the current, the E.M.F. is only 0.16 volt, after it has passed for a few seconds it rises to 1.89 volts, but when the circuit is broken it falls quickly. Even when the froth formed on the surface of the mercury is brushed off, the E.M.F. still remains high. When dilute sulphuric or hydrochloric acid is used instead of ammonium chloride, the E.M.F. is only 0.1 volt, and with a solution of sodium chloride the E.M.F. only attains 0.62 volts in  $12\frac{1}{2}$  minutes owing to the slow diffusion of the amalgam, for when crystals of the amalgam are transferred to the other portion of the cell, the E.M.F. rises to 2.146 volts. Potassium amalgam diffuses even more slowly than sodium amalgam. When ammonium amalgam is heated, its volume increases by an amount greater than that due to the expansion of the contained gases. The author concludes that an ammonium amalgam is first formed and then decomposes into mercury, hydrogen, and ammonia. E. W. W.

**Electrical Dispersion of some Organic Acids, Ethereal Salts, and Ten Varieties of Glass.** By K. FRIEDRICH LÖWE (*Ann. Phys. Chem.*, 1898, [ii], 66, 390—410).—The ethereal salts of the fatty acids and of benzoic acid do not show any abnormal electrical absorption or dispersion (compare Drude, Abstr., 1897, ii, 303); this is also the

case with ethylic cyanacetate, benzoylacetate, and acetoneoxalate, and some other ethereal salts examined by the author. Isopropyl alcohol and the butylic alcohols show an abnormal behaviour, and this is also probably the case with lactic acid. Ten different kinds of glass were examined, but the results are not sufficiently definite to decide whether the dispersion is normal or abnormal. H. C.

**Velocities of the Electrical Ions in Dilute Aqueous Solutions of up to One-tenth Normal Concentration at 18°.** By FRIEDRICH KOHLRAUSCH (*Ann. Phys. Chem.*, 1898, [ii], 66, 785—825).—For solutions of one-twentieth to one-tenth of the normal concentration, the conductivities of compounds composed of univalent ions, or of univalent ions in union with bivalent ions, may be calculated from the ionic velocities, which, in this case, depend for each univalent ion on concentration only. This does not hold for compounds composed of the bivalent ions only; for these last compounds, the velocities vary in each case with increasing concentration in the same regular manner from the velocities in solutions of infinite dilution, so that if  $l$  is the velocity in a solution of concentration  $n$ , and  $l_{\infty}$  the velocity at infinite dilution,  $l = l_{\infty} - Qn^{\frac{1}{2}}$ , where  $Q$  is a constant for all ions. If the conductivity is given in  $\text{cm}^{-1} \text{ Ohm}^{-1}$  and the concentrations in gram-equivalents per litre,  $Q$  has the value 213. This does not hold for the hydroxyl ions of the bases or the hydrogen ions of the acids, as the decrease in velocity with rising concentration is far more marked in these cases. The fall in the velocities of the bivalent ions is also not quite the same when these ions are in union with univalent ions, as when in union with other bivalent ions. All ions in solutions of infinite dilution have velocities entirely independent of the other ions with which they are associated. H. C.

**Conductivity Method of Studying Moderately Dilute Aqueous Solutions of Double Salts.** By JAMES G. MACGREGOR and E. H. ARCHIBALD (*Phil. Mag.*, 1898, [v], 46, 509—519. Compare *Abstr.*, 1898, ii, 366).—In the cases which the authors have investigated so far, the conductivity of solutions containing two electrolytes with a common ion is calculable by means of the dissociation theory up to a concentration of about 1 gram-equivalent per litre. The conductivity of solutions of the double sulphate of potassium and copper is similarly calculable only up to a concentration of about 0.1, and has at concentration 1 a considerably smaller value than that calculated on the assumption that no double molecules are present. The solutions of double salts have, at concentration unity, an appreciably smaller conductivity than the equivalent mixtures. The conductivities of mixtures, in molecular proportion, of solutions of zinc and copper sulphates, and of potassium and sodium sulphates are calculable within the limits of observational error up to a concentration, unity; and, therefore, the non-calculability in the case of the double salt solutions is probably not due to defective data. The differences between the observed and calculated values of the conductivity of the double salt solutions and of the equivalent mixtures, and between the observed values in these two sets of solutions, are

such as would be accounted for by the presence of double molecules in both, and their presence in slightly greater number in the double salt solutions than in the equivalent mixtures. H. C.

**Molecular Elevation in the Boiling Point of Liquid Ammonia.** By EDWARD C. FRANKLIN and C. A. KRAUS (*Amer. Chem. J.*, 1898, 20, 836—853).—The molecular elevation in the boiling point of liquid ammonia caused by dissolved substances was determined by a modified form of Beckmann's apparatus; the solvent was boiled in a small vacuum-jacketed Dewar-tube by the heat generated by passing an electric current through a platinum spiral immersed in the liquid ammonia. The vapour of the boiling solvent was not condensed, as is the case in the usual method, but was allowed to escape; the amount of solvent present after each boiling point measurement being determined by weighing the whole apparatus and its contents. It was found necessary to introduce a correction for the fall observed in the boiling point of the solvent, as the latter boiled away; details are given in the original paper. The constant of molecular elevation of the boiling point was calculated from the formula

$$\frac{\text{Grams solvent} \times \text{elevation} \times \text{mol. wt.}}{\text{Grams solute} \times 100} = \text{"constant."}$$

For dilute solutions of water, ethylic alcohol, propylic alcohol, phenol, catechol, resorcinol, quinol, cane-sugar, carbamide, pyridine, aniline, orthonitrophenol, and benzene, the values lay between 3 and 3.5; in more concentrated solutions, most of these substances gave lower values; cane sugar, however, gave higher values. Acetic acid interacts violently with liquid ammonia; the molecular elevation, calculated for acetic acid, has a value 2.0 for moderately concentrated solutions, and decreases with increasing concentration.

Although solutions of sodium nitrate, ammonium nitrate, and potassium iodide in liquid ammonia conduct electricity well, the values of the molecular elevations in the case of the dilute solutions are comparatively low; in each solution, however, a rapid increase of the constant occurs with increasing concentration, probably owing to the formation of a compound of ammonia with the salt. In the case of sodium and lithium, very low values are obtained for the molecular elevation; they vary from 1.50 for the more concentrated solutions to about 2.30 for the more dilute, and probably indicate the presence in solution of a molecule containing two atoms of the metal (compare Joannis, *Abstr.*, 1893, ii, 115). W. A. D.

**Aqueous Soap Solutions.** By LOUIS KAHLENBERG and OSWALD SCHREINER (*Zeit. physikal. Chem.*, 1898, 27, 552—566).—It has been shown by Krafft that soaps cause no elevation of the boiling point, so that the apparent molecular weight becomes infinite; he, therefore, regards them as colloids and has developed a theory regarding colloidal solutions (*Abstr.*, 1896, i, 80; ii, 468). The authors consider, however, that the apparent boiling point of the soap solution is not the true value, as the development of steam is extremely limited and little or no water can be distilled over. The 'pseudoboiling' is hence due to the formation of soap bubbles and dependent on the high surface tension, and with an increase of the heat supply the temperature



risers with increased frothing. The gelatinisation of the liquid on cooling does not suffice to establish the colloidal nature of soap, and experiments on the conductivity show that the solutions, unlike those of colloids, are conductors; the increase of conductivity with dilution is more rapid than that calculated by the dilution law, and indicates a probable decomposition into acid salt and free alkali. Cryoscopic observations with sodium oleate gave a molecular weight = 512—560, and hence indicate the presence of double molecules; for other soaps, the method is not available owing to the precipitation of the salt, and experiments on the diminution of vapour pressure led to no definite results.

L. M. J.

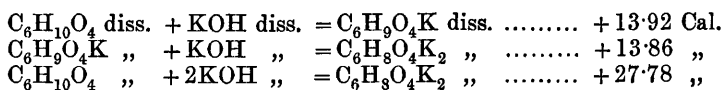
**Exact Cryometry; Application to Aqueous Solutions.** By FRANÇOIS M. RAOULT (*Zeit. physikal. Chem.*, 1898, 27, 617—661).—The question of the accuracy attainable in cryoscopic observations is fully discussed, the effects of barometric pressure and variation of the zero point are considered, and the probable errors estimated. With thermometers graduated to  $0.01^{\circ}$ , readings can be taken to  $0.0001^{\circ}$  by a telescope with micrometer eye-piece. The cold bath consists of a vessel of ether, which by a current of air may be brought to and kept at any desired temperature, and the tube containing the liquid under observation is provided with a rotatory stirrer surrounding the thermometer. The freezing point of water is taken both before and after that of the liquid, in order to eliminate errors due to barometric changes. The freezing point is taken by first overcooling the liquid to the extent of about  $1^{\circ}$ , and then inducing crystallisation by the addition of a small quantity of ice contained in a capillary tube. From the extent of overcooling, the quantity of ice formed may be calculated, and hence the correction necessary owing to the change of concentration. The external bath is so regulated that the convergence temperature is as near the actual freezing point as possible, and the author finds that the former is almost entirely independent of the atmospheric temperature but is considerably affected by variations in the rate of stirring; this is, therefore, kept constant during all the experiments. Dissolved air also influences the freezing point, and it was found that 1 c.c. of oxygen in 100 grams of water causes a depression of about  $0.0009^{\circ}$ , which indicates that oxygen, and hence, probably, nitrogen also, produces a normal depression. When all disturbing effects are eliminated and corrections applied, the author considers an accuracy of  $0.001^{\circ}$  to be readily obtainable, and that with great care an accuracy of  $0.0002^{\circ}$  may be expected. Cane sugar produces a molecular depression of 20.79 at the concentration 34.5 grams sugar to 100 grams water, and 18.7 at low concentrations; the several values lie almost accurately on a straight line, no indication being obtained of the marked decrease of molecular depression at high dilutions which has been observed by other investigators. Alcohol gave a molecular depression varying from 18.34 to 18.26, and for depressions above  $0.2^{\circ}$  the results are almost identical with those of other observers; here, however, no indication was obtained of a lower value at very dilute solutions, although this was observed by Loomis and Wildemann. The molecular depression of alcohol at infinitely

dilute solutions (18.3) is hence somewhat lower than that of cane sugar (18.7). The values obtained for sodium and potassium chlorides are also almost identical with previous values except those of Ponsot, and the author considers the method adopted by Ponsot is incapable of yielding accurate values (compare Abstr., 1894, ii, 342; 1897, ii, 88). L. M. J.

**Thermochemical Researches on Chlorinated Derivatives of the Acetic Benzoic and Salicylic Series.** By PAUL RIVALS (*Ann. Chim. Phys.*, 1897, [vii], 12, 501—574).—This is a *résumé* of thermochemical determinations which have already appeared (compare Abstr., 1895, ii, 254, 306, 483; 1896, ii, 409, 410, 588; 1897, i, 413, ii, 359; 1898, ii, 106). G. T. M.

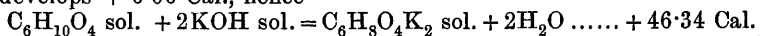
**Thermal Study of Normal Propylmalonic Acid. Heat of Formation of the Solid Potassium Salt.** By GUSTAVE MASSOL (*Compt. rend.*, 1898, 127, 1223—1224).—Anhydrous normal propylmalonic acid dissolves in water (146 grams in 2 litres) with development of heat (+3.16 Cal.).

Determinations of the heat of neutralisation of the acid with potash gave the following results.



The normal potassium salt is very deliquescent, is dried only with much difficulty, and at 135° still retains 1H<sub>2</sub>O; the desiccation is only complete after the salt has been kept for several days in dry hydrogen at 150—160°.

The anhydrous salt dissolves in water (1 gram-mol. in 8 litres) and develops +6.06 Cal., hence



This number is very close to that given by the homologous compound isoamylmalonic acid (+46.69), but is less than that of the lower homologue, ethylmalonic acid (+48.25). A. L.

**Osmotic Researches with Dilute Solutions of Cane Sugar.** By A. PONSOT (*Compt. rend.*, 1898, 125, 867).—The osmotic pressure was determined in the case of solutions of cane sugar containing 1.235 grams per litre, the method employed being the direct observation of the head of water necessary to maintain equilibrium between water and the solution separated by a semipermeable partition. With different vessels, the values obtained were 870, 873, 869, 873, and 867 mm., whilst the pressure due to a perfect gas at the same concentration is 870 mm. It hence follows that, in very dilute solutions of cane sugar, neither dissociation nor association occurs.

L. M. J.

**Osmosis of Liquids across a Membrane of Vulcanised Caoutchouc.** By G. FLUSIN (*Compt. rend.*, 1898, 126, 1497—1500).—Raoult has shown that across vulcanised caoutchouc osmosis between ether and methylic alcohol takes place in the opposite sense to that across animal membranes, and the author has extended Raoult's observa-

tions. Osmotic phenomena are not observable with water, alcohol, and acetic acid, but are marked with many organic liquids. The velocities with which the liquids examined passed across the membrane into ethylic alcohol were determined by the aid of Raoult's osmometer, and gave the following descending order: carbon bisulphide, chloroform, toluene, ethylic ether, benzene, xylene, petroleum, ( $D_0 = 0.720$ ), benzylic chloride, oil of turpentine, petroleum, ( $D_0 = 0.812$ ), nitrobenzene. The osmotic current between any two of these liquids was found to be in the sense indicated by their positions on the list, from chloroform to benzene, &c., but the velocity could not be deduced from their velocities relatively to alcohol. All these liquids are absorbed by caoutchouc, and the quantity absorbed in various times was determined, and showed that the velocities found above were approximately proportional, not to the total quantity absorbed, but to that absorbed during a short initial time of immersion (compare Abstr., 1895, ii, 487).

L. M. J.

**Zones of Reaction.** By ALBERT COLSON (*Compt. rend.*, 1898, 126, 1505—1508).—If the state of a dissociable system, such as chalk, be represented by temperature and volume coordinates, then a diagram detailed below may be obtained. If the pressure is above the dissociation pressure, there is a line  $ABCD$  almost parallel to the temperature axis, but if the gas is withdrawn at its dissociation pressure, then at the temperature of  $B$  the volume increases along  $BM$  parallel to the volume axis. The length of  $BM$  decreases with rise of temperature, so that the end  $M$  lies on a curve  $LMN$  which approaches  $ABCD$  and may be considered to meet it at a sufficiently high temperature which the author terms a chemical critical temperature and which is the analogue of the ordinary critical temperature. Hence the space is divided into a number of zones by the lines  $ABCD$ ,  $BM$ , and  $LMN$ , namely, an 'equilibrium zone,' between these lines, a 'zone of complete decomposition' outside  $LMN$ , and a 'zone of complete restitution' below  $BM$ . If, however, in the dissociated system the temperature is rapidly lowered sufficiently, the products do not again combine, so that the lower portion of the restitution zone becomes a passivity zone, and this passive zone probably occurs in many reactions, so that it is necessary for the system to attain a certain 'reaction point' before any change can occur.

L. M. J.

**Reaction Between Silver Acetate and Sodium Formate. A Reaction of the Third Order.** By ARTHUR A. NOYES and GEORGE J. COTTE (*Zeit. physikal. Chem.*, 1898, 27, 579—585).—The reaction may be represented by the equation  $2\text{AgC}_2\text{H}_3\text{O}_2 + \text{HCO}_2\text{Na} = 2\text{Ag} + \text{CO}_2 + \text{HC}_2\text{H}_3\text{O}_2 + \text{NaC}_2\text{H}_3\text{O}_2$ , or  $2\text{Ag}' + \text{HCO}'_2 = 2\text{Ag} + \text{CO}_2 + \text{H}'$ ; from this, it appears to be a trimolecular equation, and determinations of the reaction velocity showed that in a series of experiments with different initial concentrations the values of  $C_3$  were far more constant than those of  $C_2$  and remained more constant during the course of each experiment. The reaction must hence be considered to be of the third order.

L. M. J.

**Equilibrium in Precipitates.** By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1898, 19, 81—96).—If a small quantity of silver nitrate

is added to a solution containing chloride and bromide of potassium, the precipitate contains both silver bromide and silver chloride, and the author investigated the relation between the composition of the solution and that of the precipitate. Preliminary experiments showed that the composition of the precipitate changes after precipitation, and the final composition is the same as that produced when the silver nitrate is added to one of the halogen salts and the second haloid added after precipitation. Equilibrium is hence ultimately attained between the precipitate and solution. In all the experiments, 100 c.c. of N/10 silver nitrate was added to a litre of solution containing from 0.1 to 400 millimolecules of potassium bromide and from 1010 to 610 millimolecules of potassium chloride, so that the final liquid was always normal with respect to the halogens. The ratio  $\text{AgBr}/\text{AgCl}$  in the precipitate was found to increase from 0.0065 to 308.5 and the ratio  $\text{KBr}/\text{KCl}$  in the solution increased from 0.000036 to 0.6395, so that the ratio of bromide to chloride is not the same in precipitate and solution, neither are the two values in a constant ratio. The value  $(\text{AgBr in precipitate})/(\text{KBr in solution})$ , however, is approximately constant as long as the concentration of the potassium bromide does not exceed about 10 millimolecules per litre. As in dilute solution the ratio of undissociated silver bromide to potassium bromide must be approximately constant, it follows that the concentration of the silver bromide in the precipitate bears a constant ratio to that in the solution, that is, the partition ratio is constant, from which it follows that the molecular complexity is the same in the two states. The author considers that the two salts are present in the precipitate in the form of an isomorphous mixture. L. M. J.

**Velocity of crystallisation.** By A. BOGOJAWLENSKY (*Zeit. physikal. Chem.*, 1898, 27, 585—600).—The crystallisation velocity for various degrees of undercooling was determined for a large number of compounds. The effect of repeated crystallisation was investigated in the case of benzil, and it was found that, after the third recrystallisation from alcohol, further purification had but little effect. Addition of sulphonal or of benzophenone produced a lowering of velocity, which the author states is greater for small than for great undercooling; the numbers and curves, however, hardly warrant any general statement. Benzil, sulphonal, picric acid, mannitol, santonin, erythritol, and anti-pyrine gave curves completely analogous to those found by Tammann and Friedländer for benzophenone, consisting of (1) an ascending portion in which the velocity increases with the undercooling; (2) a horizontal portion in which the velocity is constant, and (3) a portion where the velocity rapidly decreases. The extent of undercooling at which a constant velocity is reached varied from about 20° to 60°. With menthol, dinitrophenol, benzoin, and coumarin, the constant value was not attained, whilst for some compounds the velocity never is constant, but reaches a maximum and then decreases. This was the case with cotoin, salipyrine, trichlorolactic acid and peucedanin (*Abstr.*, 1897, ii, 444; 1898, ii, 425). L. M. J.

**The Taste of Salts.** By RUDOLF HÖBER and FRIEDRICH KIESOW (*Zeit. physikal. Chem.*, 1898, 27, 601—616).—The authors

estimated the concentrations at which a salt taste is first observable in solutions of sulphate and chloride of potassium, sulphate, chloride, bromide, and iodide of sodium, and magnesium chloride. The concentrations of anion, cation, and undissociated molecule were then calculated at the found concentrations of the salt. In all the above cases, the anion concentration remained approximately constant, so that the salt taste is due to the anion. Analogous results were obtained with salts of ammonia and amines, but no saline taste was found with magnesium sulphate, it being completely hidden by the bitter taste. Solutions of beryllium sulphate and chloride have a sweet taste at equal cation concentrations, so that the actual taste appears to be due to both ions and possibly also in part to the undissociated molecule. For a number of hydroxyl compounds, it was found that a sweet taste was first observable when the concentration of the OH ions reached about 0.006—0.009 gram per litre.

L. M. J.

**Recalculation of Atomic Weights by the Method of Limiting Density.** By DANIEL BERTHELOT (*Compt. rend.*, 1898, 126, 1501—1504).—The author has previously pointed out that the molecular weights of gases are proportional to their densities at infinitely small pressure, and that these may be calculated from compressibility data. The atomic weights of hydrogen, nitrogen, and carbon had been thus calculated from the limiting density of their oxides, and the results are in accord with the best chemical determinations (*Abstr.*, 1898, ii, 502). Further calculations are given, the compound the density of which is employed being added in brackets: Carbon (acetylene), 12.0025; (carbonic anhydride), 12.000; (carbon monoxide), 12.007, probable value, 12.005. Nitrogen (nitrous oxide), 14.000, probable value, 14.005. Argon (from Rayleigh's determinations), mol. wt. = 39.882. Chlorine (hydrogen chloride), 35.479, identical with that obtained from Stas' analysis of silver chlorate if the value  $Ag = 107.912$  is accepted. Sulphur (sulphurous anhydride), 32.046; that resulting from Stas' analysis of silver sulphate is 32.045 if  $Ag = 107.912$ . The physical method hence appears, where applicable, to be capable of great accuracy, and the author's method of calculation is fully justified.

L. M. J.

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## Inorganic Chemistry.

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**Structural Isomerism in Inorganic Compounds.** By ARTHUR HANTZSCH (*Zeit. anorg. Chem.*, 1898, 19, 106—108).—Sabanéeff has proved the existence of certain isomeric ammonium and hydrazine salts (*Abstr.*, 1898, ii, 577) and the author points out that his statement that structural isomerism is absent among inorganic compounds does not apply to such cases, many similar isomeric compounds

having been found by Werner and others. The isomerism in all these is due to the union of different distinct groups, not to different arrangements in one group. His statement is more definite if the words 'inorganic compound' be replaced by "inorganic non-electrolyte or ion."

L. M. J.

### Specific Gravity of Liquid Air and of other Liquefied Gases.

By ALBERT LADENBURG and C. KRÜGEL (*Ber.*, 1899, 32, 46—49. Compare Cailletet and Matthias [Abstr., 1886, 758], Wroblewski [Abstr., 1884, 14, 388; 1886, 661], Olszewski [Abstr., 1884, 816; 1887, 694]).—Glass rods, the sp. gr. of which were previously determined by weighing in air and in water at 4°, were carefully weighed in liquid air and the decrease in weight noted, a Mohr's balance being employed. Corrections to weight in a vacuum were not made, neither were corrections for the expansion of glass introduced, as the coefficient of expansion at low temperatures is not known. In addition to taking the sp. gr., the authors have also determined the composition of the liquid air, and the following results have been obtained.

1. Freshly liquefied air, sp. gr. 0.9951; per cent. of oxygen, 58.83.

2. After remaining for several hours, sp. gr. 1.029; per cent. of oxygen, 64.2.

3. After standing for 2—3 days, until most of the nitrogen had evaporated, sp. gr. 1.112; per cent. of oxygen, 93.6.

Using these data, the authors have calculated the sp. gr. of a liquid air containing 20.9 per cent. of oxygen, and find it to be 0.87—0.90.

Liquid oxygen itself has a slightly lower sp. gr., namely, 1.105—1.108, than the mixture (3) containing 93.6 per cent. of oxygen.

The melting point of ethylene has been found to be  $-169^{\circ}$ , and the boiling point  $-105.4^{\circ}$  at 760 mm. pressure; Olszewski gives the same melting point, but  $-102.5^{\circ}$  as the boiling point. The sp. gr. = 0.6585 at  $-169^{\circ}$ , and = 0.571 at  $-105.4^{\circ}$ .

J. J. S.

**Liquid Ammonia as a Solvent.** By EDWARD C. FRANKLIN and C. A. KRAUS (*Amer. Chem. J.*, 1898, 20, 820—836. Compare Gore, *Proc. Roy. Soc.*, 1873, 21, 140).—The author has determined the solubility in commercial liquid ammonia of 175 metallic salts and 250 carbon compounds; his results may be summarised as follows. The alkali metals, lithium, sodium, potassium, rubidium, and caesium, are easily soluble in liquid ammonia, as well as the elements iodine, sulphur, phosphorus, and selenium; copper is slowly acted on by the solvent, especially in presence of air. Metallic fluorides appear to be mostly insoluble, and the same is true of the chlorides of the alkali metals; several of the chlorides of the heavy metals, however, are readily soluble, whilst the chlorides of magnesium, calcium, strontium, barium, zinc, cadmium, manganese, cobalt, nickel, and lead are acted on by liquid ammonia with considerable development of heat, to form insoluble additive products. Metallic bromides are more soluble than the corresponding chlorides, whilst the iodides are mostly very easily soluble; the iodides of magnesium, zinc, and cadmium, like the corresponding chlorides, appear to combine with liquid ammonia to form additive products, although these are much more soluble than those obtained in the case of the chlorides. Sulphates, sulphites, carbonates,

oxides, hydroxides, phosphates, oxalates, arsenates, ferrocyanides, and ferricyanides are insoluble in liquid ammonia, and the same is true of the sulphides with the exception of ammonium and arsenious sulphide; cyanides, cyanates, thiocyanates, and nitrates are, as a rule, easily soluble.

Although the paraffins do not dissolve in liquid ammonia, their halogen derivatives are, as a rule, readily soluble, but the solubility diminishes as the complexity of the hydrocarbon radicle is increased. Although the lower alcohols are miscible with liquid ammonia, cetylic alcohol is insoluble; diethylic ether is easily soluble, but diamylic ether dissolves only sparingly. Ethylenic glycol and glycerol are miscible with ammonia, whilst erythritol, dulcitol, and mannitol are only slightly soluble. The simpler aldehydes and their derivatives, the lower fatty acids and their halogen- and hydroxy-substituted products, and the ethereal salts are easily soluble, although the solubility decreases in each series with increasing molecular weight. Dibasic acids, and their hydroxy-derivatives, are very sparingly soluble, whilst the sugars, nitriles, cyanates, thiocyanates, amines, amido-acids, acid amides, and ureides are generally readily soluble.

Aromatic hydrocarbons and their halogen derivatives, are, as a rule, only slightly soluble in liquid ammonia, although benzene is dissolved to the extent of 10 per cent.; the nitro-derivatives of the hydrocarbons are moderately soluble, whilst most amido-derivatives dissolve very readily, although the secondary and tertiary aromatic amines are only slightly soluble. The phenols and their ethers, together with their substituted derivatives, the aromatic alcohols, aldehydes, acids, substituted acids, sulphonic acids, ethereal salts, and acid amides and anilides, are all easily soluble. The dibasic acids are, however, insoluble, and the same is true of derivatives of the terpenes; naphthalene and isoquinoline are slightly soluble, whilst the naphthols, naphthylamines, pyridine and quinoline are easily soluble.

Benzene, metaxylene, triphenylmethane, naphthalene, chloro- and iodo-benzene, dibromobenzene, and parahydroxybenzoic acid, which are all very slightly soluble in liquid ammonia at  $-38^{\circ}$ , are easily soluble at  $25^{\circ}$ . Anthracene, pinene, stearic acid, cadmium iodide, and potassium chromate are, however, insoluble, whilst phthalic and succinic acids are disintegrated at  $25^{\circ}$  and their ammonium salts formed, although these remain undissolved.

W. A. D.

**Solubility of Salts. III. The Solubility of some Metallic Nitrates.** By ROBERT FUNK (*Ber.*, 1899, 32, 96—106).—The various hydrates formed, their melting points, and the range of temperature over which each has been examined, are shown in the following table.

Cadmium nitrate, unlike the others which have been examined, crystallises at the ordinary temperature with  $4\text{H}_2\text{O}$ ; the curve for the hydrate with  $9\text{H}_2\text{O}$  extends from  $-13^{\circ}$  to  $+1^{\circ}$ , whilst that for the hydrate with  $4\text{H}_2\text{O}$  extends from  $0^{\circ}$  to the melting point at  $59.5^{\circ}$ . The cryohydrate is formed at  $-16^{\circ}$ . The curve of solubility for the hydrate of magnesium nitrate with  $6\text{H}_2\text{O}$  shows a well marked point of inflexion at  $90^{\circ}$ ; a comparison of the temperature of formation and



Nitrate.	Cryo- hydrate.	9H <sub>2</sub> O.	6H <sub>2</sub> O.	2H <sub>2</sub> O.
Magnesium.....	-29°	-23° to -18°	-18° to +67° m. p. 40°	
Zinc.....	-29°	-25° to -18°	-18° to +33·5° m. p. +36·4	+37° to +45·5° m. p. 45·5°
Manganese .....	-36°		-29° to +25·5° m. p. +25·8	27° to 35·5° m. p. 35·5°
Ferric .....	-28°	-27° to -15·5°	-9° to +60·5° m. p. 60·5°	
Cobalt.....	-29°	-26° to -20·5°	-21 to +56° m. p. 56°	+55° to 91° m. p. 91°
Nickel.....	-27°	-23° to -10·5°	-21° to +56·7° m. p. 56·7°	+58° to 95° m. p. 95°
Copper .....	-24°	-23° to -20°	-21° to +26·4° m. p. 26·4	+25° to 114·5° m. p. 114·5°

composition of the cryohydrates shows that the amount of water contained in the "cryohydrate" varies directly with the temperature at which the latter is formed.

A. H.

**Relations among the Hydrates of the Metallic Nitrates.** By J. H. KASTLE (*Amer. Chem. J.*, 1898, 20, 814—819).—It is pointed out that most of the hydrates of the metallic nitrates contain either 3, 4, 6, 9, or 12 H<sub>2</sub>O, and that in by far the greater number of these salts the number of molecules of water is some simple multiple of three. Assuming Armstrong's view (*Proc.*, 1891, 118) that, in the formation of salts, a direct addition of the acid to the base first occurs, and that subsequently an intramolecular rearrangement takes place, often accompanied by a separation of water, the author suggests that the hydrates of the nitrates are formed by a direct combination of acid and base, without the aforesaid separation of water taking place. As examples of this type of action are adduced the hydrates, CaSO<sub>4</sub> + 2H<sub>2</sub>O, BaCl<sub>2</sub> + 2H<sub>2</sub>O, and HgNO<sub>3</sub> + H<sub>2</sub>O, whose composition corresponds exactly with the sum of the acid and the base entering into action. In extending this view, the hydrates of the metallic nitrates are divided into several classes, according as they are considered to be derived from one or other of the hypothetical nitric acids, N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, H<sub>3</sub>NO<sub>4</sub>, H<sub>5</sub>NO<sub>5</sub>, &c. The anhydrous nitrates, by this hypothesis, are looked on as the additive products of the action of nitric anhydride and metallic oxides.

W. A. D.

**Metallic Phosphides and Arsenides.** By ALBERT GRANGER (*Chem. Centr.*, 1898, ii, 1004; from *Arch. Sci. phys. nat. Genève*, [iv], 6, 391—393. See Abstr., 1898, ii, 474).—By the action of arsenic trichloride on metals, arsenides are prepared analogous to the phosphides obtained by the action of phosphorus trichloride on the same metals.  
E. W. W.

**Silicon and Metallic Silicides.** By ÉMILE VIGOUROUX (*Ann. Chim. Phys.*, 1897, [vii], 12, 5—74 and 153—196).—These papers contain an historical introduction, and a detailed account of the author's contributions to the chemistry of amorphous and crystalline silicon and metallic silicides which have been previously published (compare Abstr., 1895, ii, 222, 263, 264, 447; 1896, ii, 176, 249, 362, 600).

G. T. M.

**The Newly Discovered Gases, and their Relation to the Periodic Law.** By WILLIAM RAMSAY (*Ber.*, 1898, 31, 3111—3121).—A lecture delivered before the German Chemical Society on Dec. 19th, 1898.—It is possible that a group of elements may exist between the N, P, &c., and Li, Na, &c., groups of the periodic system; these would be He=4, ?=20, A=40, &c. In the hope of obtaining the second member of this group, 15 litres of argon was examined, with a view to ascertain whether some lighter gas is not contained in it. The argon was obtained by working up a large quantity of air in the usual way; the apparatus was on a large scale, however, iron tubes of 5 cm. diameter and gasometers of 200 litres capacity being employed; the smaller gasometers, employed to hold the gas when it had become rich in argon, were constructed so that the cylindrical upper part rose and fell in a narrow, ring-shaped trough filled with water, in order to diminish the volume of water with which the argon came in contact, and the consequent loss of the gas by dissolution. The air was first passed over heated copper to remove oxygen; then twice in succession over heated magnesium to remove nitrogen, followed by heated copper oxide to remove hydrogen that had been formed; finally, in order to remove the remaining nitrogen, the gas was passed backwards and forwards over a red-hot mixture of lime and magnesia, followed by copper oxide and drying tubes. The argon was then introduced into a Dewar's tube cooled with liquid air boiling under a pressure of 10—15 mm., and there liquefied; about 25 c.c. of a clear liquid was obtained, with some solid flakes floating in it. The pressure on the boiling air was then allowed to rise, when the argon boiled off; the first small fraction was collected in a mercury gasometer; the bulk was returned to the larger gasometer, and the small, least volatile part, which volatilised but slowly from the solid residue, was collected apart. The last substance is named *metargon*; it has been but little examined as yet, nor has it been freed from argon; it exhibits the "Swan-spectrum," namely, that of carbonic oxide, when mixed with oxygen and sparked over caustic potash. The first, most volatile, fraction was again cooled with liquid air; a portion would not liquefy, and this was found to contain a new gas, *neon*, with a density of about 9.65, mixed with helium and argon. In order to separate these, enough oxygen was added to make four-fifths of the mixture liquefy

when cooled with boiling liquid air; the unliquefied part, rich in helium, was collected apart; so also the last fraction containing neon and argon, whilst the middle fraction, after removal of the oxygen by red hot copper, was moderately pure neon, still containing some helium and argon, however. It had a density = 10.04, or after sparking with oxygen in presence of caustic potash, 10.19; its refractive power as compared with air was 0.338, and its spectrum exhibited the following lines, amongst others—red, 6402, 6383, 6335, 6227, 6218, 6164, 6143, 6096, 6074, 6030; yellow ( $D_5$ ), 5853; green, 5401, 5341, 5331; blue, 4716, 4722, 4710, 4709, 4704. Assuming that neon has 1.67 as the ratio of its specific heats, it is an element, and its atomic weight, as indicated by the density 10, will be 20, so that it is, in fact, the element sought for belonging to the periodic group mentioned above.

The middle fraction obtained in the original fractional distillation of the liquid argon was fractionated twice more in the same way, the middle and by far the largest, fraction being collected each time; finally, this fraction was liquefied, boiled, and collected in 6 fractions, the density and refractivity of which were severally measured; these were the same in the case of all the fractions except the first; their values, density = 19.96 and refractive power = 0.968, may be regarded as the true values for pure argon.

The last portion that boiled off from the liquid air used for liquefying the argon was collected separately; after removal of the oxygen, the residue was not pure argon, for it was found to have the density 22.50, it had 1.66 as the ratio of its specific heats, and exhibited three brilliant lines in the red, yellow, and green (5570) respectively. The new element, the presence of which was thus indicated, was named *kyrpton*. A third gas, accompanying argon in air, has also been obtained in an impure state, when its density was 32.5 (an element with density of 40.5—41.5, and atomic weight 81—83, would occupy a place in the helium group, coming between bromine and rubidium in the periodic series). This gas is named *xenon*; it is present in so small amount in air that it could not be detected in the 15 litres of argon, but only in the large quantity of liquid air used; its spectrum exhibits many lines, but none of these are brilliant.

In order to see if any compound of argon with magnesium had been formed during the isolation of the argon from air, 700 c.c. of the magnesium nitride was treated with water in an exhausted flask, the ammonia evolved being absorbed in acid; of other gases, only 50 c.c. was obtained, consisting mainly of hydrogen with a little nitrogen and a trace of hydrocarbon and argon. The magnesia formed was extracted with water, the solution evaporated, and the residue treated with sulphuric acid in an exhausted flask; the gas evolved consisted entirely of carbonic anhydride.

C. F. B.

**Electrolysis of the Alkali Chlorides.** By F. WINTERER (*Zeit. Elektrochem.*, 1898, 5, 10—15 and 49—51).—The behaviour of different kinds of carbon when employed as anodes in the electrolysis of solutions of alkali chlorides is discussed. The formation of oxygen at the carbon anode and consequent production of carbonic anhydride is regarded as due to the decomposition of water by the chlorine

condensed in the pores of the carbon. The greater the amount of hydrochloric acid present in the electrolyte, the less oxygen is evolved. Numerous experiments are described in which a solution of potassium chloride is electrolysed with a carbon anode, an iron cathode, and a porous porcelain diaphragm. The anodic liquid is always found to contain free hydrochloric acid, but neither hypochlorous nor chloric acid. The chlorine evolved contains about 5 per cent. of impurity, mainly oxygen and carbonic anhydride, with a trace of carbonic oxide. If it is attempted to increase the concentration of the caustic potash formed in the cathode compartment beyond about 8 per cent., the current efficiency falls below 70 per cent. By using a double diaphragm, a higher concentration of the caustic alkali may be attained, together with good current efficiency, but at the cost of a higher E.M.F.

A number of samples of commercial electrolytic potassium chlorate were examined for perchlorate with negative results. T. E.

**Electrolysis of Alkali Chlorides.** By H. WOHLWILL (*Zeit. Elektrochem.*, 1898, 5, 52—76).—The E.M.F. required to separate each of the anions which may occur in alkaline solutions of the alkali chlorides during electrolysis, is determined by the method described by Glaser (this vol., ii, 78). A large, platinised platinum cathode saturated with hydrogen is employed throughout. In normal sodium hydroxide solution, the hydroxyl ion is discharged at 1.69 volts, whether the solution contains sodium chloride or not. The chlorine ion is separated from a solution containing  $1\text{NaCl} + 0.01\text{NaOH}$  (in gram-molecules per litre) at 2.07 volts, and from a solution containing  $1\text{NaCl} + 0.001\text{NaOH}$  at 2.00 volts. These numbers are in good agreement with those calculated from the E.M.F. of the chlorine-hydrogen gas cell and the dissociation of pure water, namely, 2.01 and 1.96 respectively. Chlorine is, therefore, a primary product of the electrolysis. When sodium hypochlorite is added to the solution, no new decomposition point is found, the  $\text{ClO}$  ion being probably oxidised before its discharge point is reached, the reaction being  $2\overline{\text{ClO}} + \overline{\text{OH}}(+ +) = \text{HClO}_3 + \text{Cl}$ . The  $(+ +)$  sign indicates that two positive charges of electricity are required. From a solution containing  $0.01\text{NaOH} + 1\text{NaClO}_3$ ,  $\text{ClO}_3$  ions are liberated with 2.36 volts. With small E.M.F.'s, a decomposition point corresponding with the separation of  $\overline{\text{O}}$  ions is found at 1.08 volts, and another of unknown significance between 1.36 and 1.42 volts; the two latter are not well marked. In the electrolytic experiments described, the conditions are kept as simple as possible by passing small currents for short periods of time at a definite E.M.F., by keeping the cathode and anode solutions separate, and by taking the composition of these such that it shall not be much changed by the products of the electrolysis (20 per cent.  $\text{NaCl} + 4$  per cent.  $\text{NaOH}$ ). The hydrogen electrode is always used as cathode. Beginning with the smallest E.M.F. with which a continuous current can be maintained (about 1.2 volts), the yield of hypochlorite is almost equal to the theoretical amount; with higher E.M.F.'s, it falls off rapidly, reaching 40 per cent. at 1.3 to 1.4 volts, and 2.23 per cent. at 1.44 to 1.5 volts. This initial formation of hypochlorite is attributed to the reaction  $\overline{\text{Cl}} + \overline{\text{O}}(+ +) = \text{ClO}$ . The

rapid fall in the yield of hypochlorite at 1.4 volts, and the occurrence of a decomposition point at this E.M.F., show that some new change takes place here, possibly  $\text{ClO} + \text{O}^{++} = \text{Cl} + \text{O}_2$ . As a matter of fact, a solution of sodium hypochlorite diminishes in strength if electrolysed with 1.43 volts. Chlorate is formed with 1.8 volts and upwards. The total yield of chlorate and hypochlorite then increases with the E.M.F., the ratio of hypochlorite to chlorate diminishing. When the solution is allowed to flow slowly over the anode, the total yield of hypochlorite and chlorate, as well as the relative amount of hypochlorite, is increased. Further, if the electrolysis of the same solution is continued, the yield of chlorate increases, whilst that of hypochlorite diminishes. These results confirm the conclusion drawn from the decomposition curves, namely, that the formation of hypochlorite is due to the secondary, chemical action of chlorine on the alkali present, the chlorate being formed from it in the way represented by the equation  $2\text{ClO} + \text{OH}^{++} = \text{HClO}_3 + \text{Cl}$ . T. E.

**Influence Exercised by Temperature and by certain Metallic Oxides in the Formation of Sodium Sulphate from Sulphurous Anhydride, Air, and Sodium Chloride.** By JEAN KRUTWIG and A. DERNONCOURT (*Rec. Trav. Chim.*, 1898, 17, 349—358).—The authors have extended the observations described in a former paper (*Abstr.*, 1898, ii, 24) by studying the influence of temperature, measured by a Le Chatelier's pyrometer, on the changes there considered. In one series of experiments, 1.097 grams of iron pyrites was heated in a hard glass tube with 2.028 grams of sodium chloride and 4.0 grams of ferric oxide during 3—4 hours at fixed temperatures between 350° and 750°, whilst a current of air (6—11.5 litres) was passed through the tube. A curve is given which indicates that the transformation of the sodium chloride into sulphate increases regularly with the temperature between 350° and 525°, the yield being then a maximum (71.01 per cent.). Above 525°, the yield of sulphate diminishes, albeit somewhat irregularly, until, at 750°, it amounts only to about 32 per cent. In a second series of experiments, in which the quantity of ferric oxide was doubled, the influence of temperature appeared to be somewhat irregular between 410° and 650°, the yield of sulphate being a maximum (74.8 per cent.) at 490°. Comparing the experiments of the first series with those of the second, it appears that, under equal conditions of temperature, an increase in the amount of ferric oxide is accompanied by an increase in the conversion of chloride into sulphate; in both series, the conversion is a maximum at about 500°. Attention is drawn to the fact that if, in these experiments, amorphous ferric oxide is employed, it is converted into a crystalline modification consisting of small, lustrous scales.

When the ferric oxide in the two series of experiments above described is replaced by an equal weight of cupric oxide, a much more complete conversion of chloride into sulphate is effected, although the temperature at which this is a maximum remains unchanged. In the first series, the yield (73—71 per cent.) varies little between 330° and 450°, although it shows a marked decrease at 510° (57.5 per cent.), followed by a slight but regular increase as the temperature is

raised to  $650^{\circ}$  (64.2 per cent.); in the second series, there is little difference in the amount of conversion at temperatures between  $360^{\circ}$  (95.5 per cent.) and  $640^{\circ}$  (98.2 per cent.).

Two experiments, using ferric and cupric oxides respectively, were carried out at  $350^{\circ}$ , oxygen being used to replace the air in the above method; the yield of sulphate in each case was thereby greatly increased.  
W. A. D.

**Displacement of Metals by Hydrogen.** By ALBERT COLSON (*Compt. rend.*, 1898, 127, 961—963).—Silver phosphate is slowly attacked by dry hydrogen in the dark at the ordinary temperature, with liberation of phosphoric acid and metallic silver. The action is greatly accelerated by increase of temperature, and the metal liberated at  $100^{\circ}$  is white instead of black; pressure also accelerates the change. Silver pyrophosphate is not attacked at the ordinary temperature, but reduction takes place slowly at  $100^{\circ}$ . Silver sulphate is not affected at  $100^{\circ}$ , but the change begins at about  $125^{\circ}$ , and its rate increases with rise of temperature. Silver hydroxide is attacked at the ordinary temperature. The action of hydrogen seems to be unaffected by simultaneous exposure to light.

Cupric sulphate is not attacked by hydrogen at the ordinary temperature, but absorption of the gas begins at about  $250^{\circ}$ . C. H. B.

**Silver Bisulphide.** By ARTHUR HANTZSCH (*Zeit. anorg. Chem.*, 1898, 19, 104—105).—Silver bisulphide,  $\text{Ag}_2\text{S}_2$ , is obtained by adding a solution of sulphur in carbon bisulphide to a solution of silver nitrate in benzonitrile; the precipitate, after remaining for 24 hours in a closed flask, is washed with benzonitrile and carbon bisulphide, and then with alcohol and ether, and quickly dried on a porous plate. It is a brown, amorphous powder which oxidises very rapidly when damp, yields a solution of silver sulphate when shaken with water, and does not lose sulphur when extracted with carbon bisulphide; it melts to a red liquid when heated, and then gives off sulphur and sulphurous anhydride, leaving a residue of metallic silver. When treated with dilute hydrochloric acid, it yields sulphur, hydrogen sulphide, and silver chloride, whilst nitric acid dissolves it with liberation of sulphur. Silver bisulphide can only be prepared from a solution of benzonitrile; when other solvents are used, silver sulphide is obtained.

When a solution of silver nitrate in benzonitrile is treated with ammonia, a precipitate of silverdiammine nitrate,  $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ , is obtained.  
E. C. R.

**Preparation of Thioantimonites and Thioarsenites of Silver, Copper, and Lead by a Dry Method.** By HERMANN SOMMERLAD (*Zeit. anorg. Chem.*, 1898, 18, 420—447).—The details of the method employed for the preparation of these compounds have already been described (*Abstr.*, 1897, ii, 500).

The compound  $\text{Ag}_5\text{SbS}_4$ , obtained by heating a mixture of silver chloride and antimony sulphide in the proportion  $15\text{AgCl} : 4\text{Sb}_2\text{S}_3$ , is black, has the sp. gr. = 6.100, and shows the same chemical reactions as pyrrargyrite and miargyrite. The product obtained

by melting a mixture of silver sulphide and antimony sulphide is iron black and has the sp. gr. = 6.173.

Artificial polyargyrite is obtained by melting silver chloride and antimony sulphide in the proportion  $24\text{AgCl} : 5\text{Sb}_2\text{S}_3$  and then reheating the melt with more antimony sulphide; the product is of a dark lead grey colour, gives a red powder, and has the sp. gr. = 5.730 (the sp. gr. of natural polyargyrite = 6.974). It is also obtained by melting a mixture of silver sulphide and antimony sulphide, when a dark iron grey ductile mass of sp. gr. = 6.500 is obtained.

Artificial proustite, prepared by fusing its components together, is similar to the product obtained from silver chloride and arsenic sulphide, which has already been described. The compound  $\text{AgAsS}_2$  is obtained by heating a mixture of silver chloride and arsenic sulphide in the proportion  $3\text{AgCl} : 2\text{As}_2\text{S}_3$ , when the reaction commences at  $170^\circ$  and is completed by heating with the bare flame; the product is a reddish-black, crystalline substance which gives a brownish-red powder, and has the sp. gr. = 4.700. When subjected to prolonged heating at a high temperature, it is converted into a substance having the appearance and properties of proustite.

Silver pyrothioarsenite,  $\text{Ag}_4\text{As}_2\text{S}_5$ , is obtained by carefully heating a mixture of silver chloride and arsenic sulphide in the proportion  $12\text{AgCl} : 5\text{As}_2\text{S}_3$ . The product, a lustrous, black mass of sp. gr. = 4.886, has a conchoidal fracture, gives a dark red streak and powder, and reacts with acids and alkali sulphides in the same way as proustite. When cautiously heated, it melts without evolution of arsenic sulphide, and when heated for some time in a current of hydrogen sulphide, is converted into a reddish-black melt having the composition of proustite. The compound  $\text{Ag}_5\text{AsS}_4$ , obtained by melting its components, is an iron grey, crystalline mass having the sp. gr. = 5.517, but when prepared from silver chloride and arsenic sulphide, it has the sp. gr. = 5.547. The compound  $\text{Ag}_{24}\text{As}_3\text{S}_{15}$ , obtained by melting silver sulphide with arsenic sulphide ( $12\text{Ag}_2\text{S} : \text{As}_2\text{S}_3$ ), is a crystalline, black mass of sp. gr. = 6.279 which melts without evolution of arsenic sulphide, and is decomposed by hot solutions of potassium hydroxide and alkali sulphides. The author was unable to obtain this compound from silver chloride and arsenic sulphide.

Artificial wolfsbergite,  $\text{CuSbS}_2$ , is obtained on heating a mixture of cuprous chloride and antimony sulphide in the proportion  $3\text{CuCl} : 2\text{Sb}_2\text{S}_3$ , the reaction commencing at  $130^\circ$ , but requiring a high temperature to complete it. The product is a steel grey, crystalline melt with a slight copper lustre, is easily broken into a black powder, and has the sp. gr. = 4.885 (natural wolfsbergite has the sp. gr. = 4.7—4.8). It is easily melted when heated in a glass tube, gives a clear solution with nitric acid in the presence of tartaric acid with precipitation of sulphur, and is not attacked by ammonia, but is decomposed by hot potassium hydroxide or alkali sulphides. The product obtained by melting a mixture of copper sulphide and antimony sulphide is similar and has the sp. gr. = 4.979. Artificial guejarite,  $\text{Cu}_2\text{Sb}_4\text{S}_7$ , obtained in a similar manner to the preceding compound, is very similar to artificial wolfsbergite, and has the sp. gr. = 4.814. The sp. gr. of natural guejarite = 5.03. The compound  $\text{Cu}_3\text{SbS}_3$ , obtained by melting cuprous

chloride with antimony sulphide, is a black, brittle mass, and has the sp. gr. = 5.182. The product prepared from copper sulphide and antimony sulphide has the sp. gr. = 5.113.

The author was unable to obtain copper thioarsenites of definite composition. When a mixture of cuprous chloride and arsenic sulphide in the proportion requisite for the formation of binnite,  $\text{Cu}_6\text{As}_4\text{S}_9$ , is heated, reaction commences at 200—300° and arsenic chloride mixed with arsenic sulphide distils over. The product is a black mass which does not melt when heated over the free flame, has the sp. gr. = 4.289, is decomposed by acid, potassium hydroxide, and alkali sulphides, and has a composition closely approximating to that required by the formula  $\text{Cu}_4\text{As}_2\text{S}_5$ .

The preparation of thioantimonites of lead from lead chloride and antimony sulphide requires a high temperature, and only a few of them can be prepared by this method as the melt contains unaltered lead chloride after the antimony sulphide has commenced to sublime. Zinckenite and jamesonite, which, for their preparation, require the proportion of antimony sulphide to lead chloride to be about 1 : 1, are more easily prepared than boulangerite, which requires the proportion 1 : 1.2 whilst meneghinite, which requires the proportion 1 : 1.4, cannot be prepared by this method. Artificial zinckenite,  $\text{PbSb}_2\text{S}_4$ , prepared by heating a mixture of lead chloride and antimony sulphide in a blast furnace, is a steel grey, fibrous mass of sp. gr. = 5.320 (the sp. gr. of the natural mineral = 5.3) of similar appearance to antimonite, and gives a dark grey streak and powder. It is decomposed by hydrochloric acid with evolution of hydrogen sulphide, dissolves in nitric acid in the presence of tartaric acid without precipitation of lead sulphate, and is decomposed by hot potassium hydroxide and alkali sulphides. A similar product is obtained on melting a mixture of lead sulphide and antimony sulphide in an atmosphere of hydrogen sulphide, and has the sp. gr. = 5.280.

Artificial jamesonite,  $\text{Pb}_2\text{Sb}_2\text{S}_5$ , prepared in a similar manner from lead chloride, resembles the preceding compound, but is darker in colour; sp. gr. = 5.832 (the sp. gr. of the natural mineral = 5.6—5.8), but when prepared from lead sulphide and antimony sulphide, the sp. gr. = 5.750. Artificial boulangerite,  $\text{Pb}_3\text{Sb}_2\text{S}_6$ , prepared from lead chloride, is a steel grey, crystalline mass of sp. gr. = 5.871 (the sp. gr. of the natural mineral = 5.8—6.0), gives a greyish-black streak and powder, and resembles zinckenite as regards chemical behaviour. The product prepared from lead sulphide has the sp. gr. = 5.860. The product prepared by precipitating a solution of lead acetate with sodium thioantimonate and melting the precipitate in an atmosphere of hydrogen sulphide is similar to the preceding, and has the sp. gr. = 5.907. Meneghinite, geocronite, and kilbrickenite cannot be prepared from lead chloride; the melts always contain lead chloride, which cannot be completely extracted by hot water. When prepared by melting mixtures of lead sulphide and antimony sulphide in the requisite proportions, lead grey, crystalline compounds are obtained which are similar to the natural minerals. Artificial domingite,  $\text{Pb}_3\text{Sb}_4\text{S}_9$ , prepared from lead chloride, is a dark grey mass, showing on a fracture long, radiating needles, and has the sp. gr. = 5.632. A similar product



is obtained from lead sulphide, and has the sp. gr. = 5·605. Artificial pligionite,  $\text{Pb}_5\text{Sb}_8\text{S}_{17}$  prepared from lead chloride, is a lead coloured, granular melt, and has the sp. gr. = 5·500. (The sp. gr. of the monoclinic natural mineral = 5·4). The product obtained from lead sulphide is composed of slender crystals, and has the sp. gr. = 5·447.

The preparation of lead thioarsenites from lead chloride and by melting their components is difficult, since they are easily decomposed by heat with sublimation of arsenic sulphide. When lead sulphide and arsenic sulphide are melted together in the proportion required for the formation of scleroclase,  $\text{PbAs}_2\text{S}_4$ , a black, lustrous melt of the required composition is obtained; it has the sp. gr. = 4·585, is decomposed by ammonia, and gives a black streak and powder, whereas natural scleroclase gives a reddish-brown streak, and has the sp. gr. = 5·393. When the preceding product is heated in a current of hydrogen sulphide, a greyish-black, porous mass is obtained which has the sp. gr. = 5·590 and a composition closely approximating to that of dufrenoyite,  $\text{Pb}_2\text{As}_2\text{S}_5$ ; when heated at a higher temperature as long as arsenic sulphide is volatilised, a product is obtained having a composition closely approximating to that of jordanite,  $\text{Pb}_4\text{As}_3\text{S}_7$ . The author was unable to obtain artificial scleroclase from lead chloride and arsenic trisulphide; the product contains lead chloride at temperatures below that of the blast furnace, and at the higher temperatures consists of lead sulphide containing about 4 per cent. of arsenic sulphide. A product of the composition of dufrenoyite,  $\text{Pb}_2\text{As}_2\text{S}_5$ , is obtained by fusing a mixture of lead sulphide and arsenic sulphide; it is a steel grey, lustrous mass, consisting of slender needles, has the sp. gr. = 5·505, and is decomposed by ammonia. Artificial guitermanite,  $\text{Pb}_3\text{As}_2\text{S}_6$ , obtained by melting its components, is a lead grey, crystalline mass of sp. gr. = 5·860, and is similar to artificial boulangerite. Artificial jordanite,  $\text{Pb}_4\text{As}_3\text{S}_7$ , obtained by melting its components, is a lead grey product of sp. gr. = 6·101, and is not attacked by ammonia.

E. C. R.

**Calcium and Calcium Hydride.** By BÉLA VON LENGYEL (*Chem. Centr.*, 1898, ii, 262; from *Math. naturw. Ber. Ungarn*, 14, 180—188).—The author has obtained calcium by electrolysis anhydrous calcium chloride in a graphite crucible containing a porous earthenware cell, the former being connected to the positive and the latter to the negative pole by means of iron wire; a current of 10—18 amperes at 70—110 volts is employed. After removing the excess of calcium chloride by allowing the regulus to remain in anhydrous ether, a material containing 99·2 per cent. of calcium may be obtained. The metal has a sp. gr. = 1·5540 at 18°, and its properties correspond with those of Mathiessen's preparation; it has the colour of a gold alloy rich in silver, and is not affected by cold dry air, but burns with a dazzling light when heated to bright redness; it also burns in chlorine and in sulphur vapour, but combines with iodine without emitting light. From concentrated or dilute hydrochloric acid and from water, calcium liberates hydrogen, but it is not attacked by concentrated sulphuric or concentrated nitric acid unless boiled with it.

Calcium unites with hydrogen at the ordinary temperature to form

the hydride,  $\text{CaH}_2$ , and at a red heat the action is very energetic; the hydride is a greyish, earthy substance, and decomposes water more readily even than the metal, the hydrogen often inflaming. It burns in oxygen at a red heat, emitting a brilliant light, combines energetically with chlorine at a red heat, glows when heated in iodine vapour, and falls to a grey dust when heated in sulphur vapour. Towards acids, calcium hydride behaves like calcium itself, but it attacks ether with violence.

The author has not succeeded in preparing metallic barium, and finds that strontium is more difficult to obtain than calcium.

E. W. W.

**Impurities of Commercial Calcium Carbide.** By HENRI LE CHATELIER (*Bull. Soc. Chim.*, 1897, [iii], 17, 793—794).—The chief impurities of calcium carbide are silicon and iron, and a study of the state of combination in which these elements exist in the compound is interesting as affording evidence as to their relative affinities at a temperature of about  $2000^\circ$ , the point of solidification of calcium carbide. The iron is always wholly combined with silicon, and by treating the carbide with water and acids, small crystals of the silicide of iron,  $\text{SiFe}_2$ , studied by Moissan are obtained. The remainder of the silicon combines either with carbon or calcium, according to the relative proportions of the latter. If the carbon is in excess, hexagonal plates of carbon silicide, generally of a blue colour, are formed; if, however, there is an excess of calcium, calcium silicide is formed and may be obtained in the form of metallic grains having the lustre and colour of zinc. Two varieties of calcium silicide appear to exist; the one scarcely acted on by nitric acid, but readily attacked by hydrochloric acid with the formation of a yellow, insoluble substance; and the other readily acted on by nitric and acetic acids, and giving a white deposit with hydrochloric acid which, like the yellow substance, dissolves in caustic potash with the evolution of hydrogen. As a rule, on treating calcium silicide with hydrochloric acid, a mixture of the white and yellow substances is obtained, ranging in composition between  $\text{Si}_2\text{O}_4\text{H}_4$  and  $\text{Si}_2\text{O}_3\text{H}_4$ .

N. L.

**Colour of Calcium Carbide.** By HENRI MOISSAN (*Compt. rend.*, 1898, 127, 917—918).—Calcium carbide, obtained by the dissociation of the compound  $\text{C}_2\text{Ca}, \text{C}_2\text{H}_2, 4\text{NH}_3$  (this vol., i, 241) is white and transparent like the alkali carbides, whereas the calcium carbide prepared in the ordinary way in the electric furnace has an iridescent, metallic appearance, and is only partially transparent in thin layers. If, however, the materials from which the carbide is prepared are free from iron, it is also white and transparent when prepared by the action of heat on a mixture of carbon with either the metal, its hydride, or its nitride.

C. H. B.

**Electrolysis of Solutions of Calcium Chloride.** By FELIX OETTEL (*Zeit. Elektrochem.*, 1898, 5, 1—5).—The results obtained by Foerster and Bischoff (this vol., ii, 89) are confirmed by the author's experiments. If the solution of calcium chlorate obtained electrolytically is treated with potassium chloride, potassium chlorate crystallises out, and the mother liquor containing calcium chloride mixed

with a little potassium chloride may again be electrolysed. The yield of chlorate thus obtained is good at first, but quickly diminishes, much free chlorine being evolved, and solid crusts formed at the cathode. The author believes that, when pure calcium chloride is employed, lime dissolves in the form of calcium oxychloride, and that the presence of potassium chloride diminishes the solubility of this substance so much that lime cannot dissolve in sufficient quantity to combine with all the chlorine liberated at the anode. The presence of copper salts in the electrolyte brings about rapid catalytic decomposition of the hypochlorite, oxygen being evolved. Ferric oxide, lead peroxide, or nickel peroxide behave similarly. The author ascribes the formation of chlorate to two reactions; (a) the oxidation of hypochlorite, formed from chlorine and alkali hydroxide, either by chlorine or by oxygen liberated by the electrolysis, (b) the direct union of chlorine and oxygen during their simultaneous liberation at the anode. In neutral solutions, the first, in strongly alkaline solutions, the second, process is the principal one. T. E.

**Calcium and Magnesium Hydrogen Carbonates.** By KARL KIPPENBERGER (*Zeit. anorg. Chem.*, 1898, 17, 413—417), and FREDERICK PEARSON TREADWELL (*ibid.*, 418—419).—In a recent paper by Treadwell and Reuter (*Abstr.*, 1898, ii, 473), Kippenberger's views as to the existence of magnesium hydrogen carbonate were unintentionally misrepresented: he holds that it can only exist in presence of free carbonic acid (compare *Abstr.*, 1894, ii, 281).

**Electrolysis of Solutions of Zinc Chloride and the Nature of Spongy Zinc.** By FRITZ FOERSTER and O. GUNTHER (*Zeit. Elektrochem.*, 1898, 5, 16—23).—A perfectly neutral solution of zinc chloride containing 54.6 grams of zinc per litre was electrolysed with a cathodic current density of 1.4 ampères per square decimetre. The anode consisted of pure electrolytic zinc. For several hours, the deposit consisted of smooth, light-grey zinc; after 20 hours, the solution became turbid owing to the separation of zinc oxychloride, and zinc sponge was deposited. The solution then contained 1 molecule of  $\text{ZnO}$  to 14  $\text{ZnCl}_2$ . By using a small, subsidiary platinum anode, a small quantity of chlorine was continuously supplied to the solution; this did not, however, prevent the formation of the sponge. Zinc chloride solutions, whether acid or alkaline originally, always become basic after a time, owing to the energetic oxidation of the zinc electrodes by atmospheric oxygen in presence of zinc chloride, and the formation of the zinc sponge always begins when the solution is saturated with zinc oxide. From a solution containing 1/20 to 1/30 gram-molecule of hydrochloric acid per litre, zinc may be deposited in any quantity without the spongy deposit appearing. Under these circumstances, some hydrogen is evolved, the bubbles of which remain persistently attached to the cathode, producing unevenness in the deposit. The presence of a little free chlorine (0.2 gram per litre) is useful in preventing this prolonged adherence to the same point. By this method, perfect deposits of zinc, quite free from arsenic, were also obtained when impure zinc anodes were used.

Schnabel has stated that Ashcroft obtained considerably (50 per

cent.) more than the theoretical amount of zinc in the electrolysis of solutions of basic zinc salts. The authors have failed to obtain any indication of such results.

It is, finally, shown in detail that all definitely ascertained facts relating to the formation of spongy zinc point to the conclusion that it is produced whenever the condition of the solution at the cathode is such that basic zinc salts or zinc hydroxide may separate out there.

T. E.

**Solubility of Salts. II. Solubility of the Halogen Salts of Zinc and Cadmium.** By RUDOLF DIETZ (*Ber.*, 1899, 32, 90—96).—Zinc chloride forms no fewer than five different hydrates, the solubility of each of which can be determined for a certain range of temperature; numbers have been obtained for the hydrate with  $3\text{H}_2\text{O}$  from  $-5^\circ$  to  $+7^\circ$  at which it melts; for the hydrate with  $2\frac{1}{2}\text{H}_2\text{O}$  from  $0^\circ$  to its melting point at  $13^\circ$ ; for the hydrate with  $2\text{H}_2\text{O}$  from  $0^\circ$  to its melting point at  $19^\circ$ ; for the hydrate with  $1\frac{1}{2}\text{H}_2\text{O}$  from  $0^\circ$  to its melting point at  $26^\circ$ ; for the hydrate with  $1\text{H}_2\text{O}$  from  $0^\circ$  to  $27^\circ$ ; and for the anhydrous salt from  $15^\circ$  to  $100^\circ$ . Above  $23^\circ$ , the anhydrous salt is in a stable condition, whilst below that temperature it is unstable and readily passes into the modification with  $1\frac{1}{2}\text{H}_2\text{O}$ . Zinc bromide only forms two hydrates. The solubility of that with  $3\text{H}_2\text{O}$  can be followed from  $-15^\circ$  to the melting point at  $-5^\circ$ ; of that with  $2\text{H}_2\text{O}$  from  $-8^\circ$  to the melting point at  $37^\circ$ ; and of the anhydrous salt from  $33^\circ$  to  $100^\circ$ . The curve consists of three branches intersecting at  $-8^\circ$  and at  $+35^\circ$ . Zinc iodide only forms a single hydrate, which contains  $2\text{H}_2\text{O}$ , the solubility of which has been determined from  $-10^\circ$  to  $27^\circ$ , its melting point, whilst the solubility of the anhydrous salt has been determined from  $0^\circ$  to  $100^\circ$ . The curve of solubility consists of two branches, intersecting at  $0^\circ$ , the anhydrous salt being stable above this temperature. Only three hydrates of cadmium chloride, containing 1,  $2\frac{1}{2}$ , and  $4\text{H}_2\text{O}$ , have been obtained, the author having been unable to prepare those containing 2 and  $5\text{H}_2\text{O}$ . The curve for the hydrate with  $4\text{H}_2\text{O}$  extends from  $-9^\circ$  to  $+15^\circ$ ; that for the hydrate with  $2\frac{1}{2}\text{H}_2\text{O}$  extends from  $-10^\circ$  to  $+36^\circ$ ; that for the hydrate with  $1\text{H}_2\text{O}$  from  $+10^\circ$  to  $100^\circ$ . The solubility curve consists of three branches, intersecting at  $-5^\circ$  and  $+34^\circ$ . An isomeride of the hydrate with  $2\frac{1}{2}\text{H}_2\text{O}$  is deposited in compact needles when a 50 per cent. solution of the salt is evaporated over sulphuric acid, but it is so unstable that its solubility cannot be determined. Cadmium bromide only forms a hydrate with  $4\text{H}_2\text{O}$ , all attempts to prepare one with  $2\frac{1}{2}\text{H}_2\text{O}$  having proved unsuccessful; the curve for the hydrate extends from  $0^\circ$  to  $38^\circ$ ; whilst that for the anhydrous salt extends from  $35^\circ$  to  $100^\circ$ , and intersects that of the hydrate at  $36^\circ$ . Cadmium iodide is only known in the anhydrous state, the solubility increasing from 44.39 per cent. at  $0^\circ$  to 56.08 per cent. at  $100^\circ$ .

A. H.

**Dissociation of Minium.** By HENRI LE CHATELIER (*Bull. Soc. Chim.*, 1897, [iii], 17, 791—792).—The following dissociation pressures were observed, the substance being placed in a porcelain tube

heated by a platinum spiral traversed by an electric current and connected below with a glass tube dipping into mercury.

Temperature ...	455°	500°	555°	636°
Pressure.....	5 mm.	60 mm.	183 mm.	763 mm.

From these results, it appears that in air containing oxygen at a partial pressure of about 150 mm., minium cannot be formed above 550°. Oxidation takes place most rapidly at about 500°.

The allotropic transformation of lead monoxide takes place at 580°, and its melting point was found to be 830°. It is shown how the author's results explain the absorption of oxygen by melted litharge and its evolution on solidification. N. L.

**Compounds of Lead Iodide with other Iodides.** By A. MOSNIER (*Ann. Chim. Phys.*, 1897, [vii], 374—426).—The author continues the study of the double salts obtained from lead iodide and the iodides of lithium, sodium, rubidium, ammonium, tetramethylammonium, tetrethylammonium, and phenylammonium; their heats of formation are always positive, whether the salt is anhydrous or hydrated. In the case of the double iodides with calcium, strontium, and barium (compare Abstr., 1895, ii, 268), the heat of formation of the anhydrous salt is negative, whereas that of the hydrated compound is positive. A further number of double iodides have been prepared, whose heats of formation are always positive, whether determined for the anhydrous or the hydrated salt. Some of these may be arranged in groups having the following general formulæ:  $\text{PbI}_2, 2\text{MI}_2$ , where  $\text{M} = \text{Mg}, \text{Zn}, \text{or Cd}$ ;  $\text{PbI}_2, 2\text{M}_1\text{I}_2 + 3\text{H}_2\text{O}$ , where  $\text{M}_1 = \text{Fe}, \text{Mn}, \text{Cr}, \text{Ni}, \text{or Co}$ ; and  $3\text{PbI}_2, \text{RI}_3 + 12\text{H}_2\text{O}$ , where  $\text{R} = \text{P}, \text{As}, \text{Sb}, \text{or Bi}$ . Besides those included in the preceding groups, there are others such as the stannous and aluminium compounds,  $\text{SnI}_2, \text{PbI}_2 + 8\text{H}_2\text{O}$  and  $\text{Al}_2\text{I}_6, 3\text{PbI}_2 + 10\text{H}_2\text{O}$ ; the composition  $\text{Be}_2\text{I}_6(?) , 3\text{PbI}_2 + 10\text{H}_2\text{O}$  is given to the beryllium double salt. All the double iodides except those with the quaternary ammonium bases are decomposed by water. Mercuric iodide does not form a double salt with lead iodide. Although thallium and barium resemble lead in some respects, they do not form analogous series of double iodides. Some few double lead bromides resemble the corresponding iodides in composition. G. T. M.

**Metallic Triple Nitrites.** By CARL PRZIBYLLA (*Zeit. anorg. Chem.*, 1898, 18, 448—463).—A further examination of the metallic triple nitrites described by the author (Abstr., 1898, ii, 162) shows that they are isomorphous mixtures rather than true chemical compounds. Copper strontium potassium nitrite, the corresponding ammonium salt, copper calcium potassium nitrite, and others, vary in composition according to the relative amounts of the constituent salts which are present, and when recrystallised from water the composition is again altered. The author points out, however, that many of the lead compounds and others are characteristic salts which have a composition agreeing with the required formula, even when prepared from solutions containing varying proportions of their constituents; and the extremely great differences in the solubility of these salts when

compared with that of their constituents is difficult to reconcile with the view that they are isomorphous mixtures.

The following new salts are described : *Lead copper thallium nitrite*, obtained by the method previously described, is a brown powder consisting of transparent, microscopic splinters. *Copper barium thallium nitrite* is very similar to the corresponding potassium salt but more sparingly soluble. *Nickel lead thallium nitrite* and *nickel barium thallium nitrite* are obtained as brown, crystalline powders, and are strongly refractive. *Lead iron thallium nitrite* is a deep orange-red powder consisting of microscopic cubes, and is strongly refractive.

E. C. R.

**Separation of Cerium from Lanthanum and Didymium, and its Estimation in Presence of the Latter.** By P. MENGEL (*Zeit. anorg. Chem.*, 1898, 19, 67—77).—From an examination of the methods employed for the separation of cerium, the author concludes that the best method is by oxidation with sodium dioxide. The cerium solution is treated at the ordinary temperature with a solution of sodium dioxide in ice-cold water, and the reddish-brown precipitate is washed with hot water dried at 120—130°, when it turns bright brown to yellow ; it is then dissolved in strong nitric acid, and the cerium precipitated as the ammonium double salt in the usual way.

According to Cleve, the cerium earths are precipitated by ammonia and hydrogen peroxide in the form of oxides of constant composition ; but this is not the case when sodium dioxide is employed at the ordinary temperature ; oxyhydroxides are then obtained containing more oxygen than the sesquioxide and less oxygen than Cleve's peroxides, and the amount of oxygen varies with the conditions of the experiment, especially with the temperature. When a solution of a pure cerium salt is precipitated with sodium dioxide and boiled, whereby a bright yellow precipitate of cerium dioxyhydroxide is obtained, and this is dried at 130°, and the percentage of  $\text{CeO}_2$  in the precipitate estimated with ferrous ammonium sulphate and permanganate, results are obtained which show that the oxidation of the cerium is incomplete. If, however, the precipitate is heated over the blowpipe, the theoretical quantity of dioxide is obtained.

When a mixture of lanthanum and didymium salts, free from cerium, is treated with sodium dioxide in the cold, it yields a precipitate which gives off oxygen when the mixture is warmed ; the precipitate, when dried at 120°, is bluish-white, and contains much carbonic anhydride absorbed from the air, which is eliminated only by a high temperature ; when heated at 400°, it becomes dark brown, and on further heating over the blowpipe assumes the characteristic grey colour of the anhydrous sesquioxide. The brown coloration is due to the formation of a higher oxide of praseodymium, and since this higher oxide cannot be obtained by the action of chlorine in alkaline solution, the praseodymium peroxide, like barium peroxide, must belong to the type  $\text{H}_2\text{O}_2$ . The oxalates of lanthanum and didymium do not yield the brown oxide when heated ; if, however, the grey oxide which is obtained is moistened with nitric acid and cautiously heated, the brown oxide is obtained.

The estimation of cerium in admixture with lanthanum and didymium cannot be effected by determining the excess of oxygen in the precipitate obtained by means of sodium dioxide; the lanthanum and didymium oxides, when dried at  $230^{\circ}$ , still retain an excess of oxygen, and when the oxides are heated at  $400^{\circ}$ , the brown praseodymium peroxide combines with the cerium dioxide and forms a compound which is not decomposed at a white heat; consequently, the estimation of the peroxide-oxygen by means of ferrous ammonium sulphate or potassium iodide gives results higher than are required for the cerium dioxide. The same error is, of course, present when the oxides are obtained by heating a mixture of the oxalates. The estimation of cerium in the cerium earths by estimating the peroxide-oxygen in the ignited oxides gives accurate results only when a very small quantity of praseodymium is present.

E. C. R.

**Condensed Oxides of the Rare Earths.** By GRÉGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Compt. rend.*, 1898, 127, 863—866).—On adding water to a solution of cerosceric oxide,  $Ce_3O_4$ , in nitric acid, a white, gelatinous *precipitate* separates, having the composition  $Ce_3O_4 \cdot HNO_3$ ; when completely dehydrated, this resembles amber, and dissolves completely in water, giving a solution of strongly acid reaction, from which the original compound is reprecipitated on adding dilute nitric or hydrochloric acid. The oxide obtained on decomposing the compound  $Ce_3O_4 \cdot HNO_3$  by alkali is very different in character from, and is probably polymeric with, the oxide precipitated from a normal cerium salt such as the nitrate  $Ce_3(NO_3)_8$ ; when moist, it is white, but on drying becomes yellow and horn-like; hot hydrochloric acid only acts on it slowly, but nitric acid regenerates the compound  $Ce_3O_4 \cdot HNO_3$ .

It is usually stated that the oxide obtained by igniting cerium oxalate is not acted on by nitric acid, but this is only true when the temperature of ignition exceeds  $1500^{\circ}$  and the oxide obtained is perfectly white. When the calcination is carried out below  $500^{\circ}$ , a very dense, canary-yellow *modification* of the oxide  $Ce_3O_4$  is obtained, which is transformed by 2—3 per cent. nitric acid into a white, gelatinous *substance*, which readily dissolves in water. The aqueous solution has an acid reaction, is opalescent, and on adding 2 per cent. nitric acid gives a *precipitate* having the composition  $(Ce_3O_4)_5 \cdot HNO_3$ , when dried; when decomposed by alkalis, this gives an *oxide*, white when moist, yellow when dry, which is not acted on by concentrated hydrochloric acid, either alone or in presence of potassium iodide.

When solutions of the compounds  $Ce_3O_4 \cdot HNO_3$  and  $(Ce_3O_4)_5 \cdot HNO_3$  are decomposed by an excess of dilute sulphuric acid, *substances* completely insoluble in water are obtained which no longer contain nitric acid, although only half that originally present has been replaced by sulphuric acid; on this account, the authors ascribe to the original nitrates the formulæ  $(Ce_3O_4)_4 \cdot 2H_2N_2O_6$  and  $(Ce_3O_4)_{20} \cdot 2H_2N_2O_6$ , and to the sulphates derived from them the formulæ  $(Ce_3O_4)_4 \cdot H_2SO_4$  and  $(Ce_3O_4)_{20} \cdot H_2SO_4$ . On saturating half the nitric acid of either of the nitrates and adding a little ammonium nitrate, completely insoluble

*salts* are obtained which correspond with the oxide  $(\text{Ce}_3\text{O}_4)_n$ ,  $n > 20$ , derived from cerium oxalate by ignition above  $1500^\circ$ .

The oxide  $(\text{Ce}_3\text{O}_4)_{20}$  can be reduced to its simpler polymerides by the action of nitric acid at  $180^\circ$ ; it initially dissolves, giving a yellow solution from which water precipitates the nitrate  $(\text{Ce}_3\text{O}_4)_4, 4\text{HNO}_3$ , but later produces a red solution containing the normal salt  $\text{Ce}_3(\text{NO}_3)_8$ ; ultimately, a colourless solution is obtained containing only the nitrate of the protoxide. The oxide  $(\text{Ce}_3\text{O}_4)_4$ , similarly, is readily depolymerised in contact with warm nitric acid.

When thorium oxalate, nitrate, chloride or hydroxide is carefully ignited, a product is obtained which in general consists of a mixture of two polymerides of the oxide  $\text{ThO}$ ; these do not dissolve in nitric or hydrochloric acid, but combine with both to form salts soluble in water. From the aqueous solutions thus obtained, the two polymerides separate in succession on carefully adding increasingly concentrated nitric acid; the *nitrate* which first separates has the composition  $(\text{ThO})_{12}, \text{HNO}_3$ , whilst the formula of the salt separating later is  $(\text{ThO})_5, \text{HNO}_3$ , or possibly  $(\text{ThO})_4, \text{HNO}_3$ . Since these nitrates behave towards sulphuric acid in the same manner as the corresponding cerium salts described above, their formulæ seem to be respectively  $(\text{ThO})_{48}, 2\text{H}_2\text{N}_2\text{O}_6$  and  $(\text{ThO})_{20}, 2\text{H}_2\text{N}_2\text{O}_6$ .

Lanthanum and didymium oxides yield only the normal, insoluble salts,  $(\text{LaO})_4, 2\text{HNO}_3$  and  $(\text{DiO})_4, 2\text{HNO}_3$ , described by Marignac, but from yttrium are derived the normal salt  $(\text{YO})_4, 2\text{HNO}_3$ , and the acid salt  $(\text{YO})_4, 4\text{HNO}_3$ . It thus appears that the property of condensing and giving rise to acid as well as normal salts is a general property of the rare earths.

Generalising from their results, the authors suggest that the so-called "basic salts" are formed by successive polymerisation of the metallic oxide from which they are derived, this process being accompanied necessarily by a change in the valency of the oxide; the basic salts of bismuth, lead, and mercury are cited as examples.

W. A. D.

**Crystalline Double Oxides obtained at High Temperatures.** By EM. DUFAU (*Ann. Chim. Phys.*, 1897, [vii], 12, 257—288).—A *résumé* of work already published (compare Abstr., 1896, ii, 167, 524, 647; 1897, ii, 100, 145).

G. T. M.

**Properties of Aluminium.** By ALFRED DITTE (*Compt. rend.*, 1898, 127, 919—924).—It is generally believed that aluminium is not attacked by water or dilute acids, but this result is really due to the formation, at the surface of the metal, of a layer of gas which adheres strongly and prevents further access of the liquid. If this layer of gas is removed by mechanical means, or if the action takes place in a vacuum, the aluminium is completely dissolved by acetic, citric, oxalic, tartaric, and other acids. Similarly, the resistance of the metal to the action of solutions of salts, such as the halogen salts of the alkalis, which should attack it with considerable development of heat, is due to the formation of a protective film of aluminium hydroxide. If a small quantity of a dilute acid is added, the oxide is dissolved and the action of the saline solution continues. A mixture of sodium



chloride solution and dilute acetic acid, for example, will dissolve aluminium so long as any free acid remains, although neither the acid nor the saline solution would attack the metal more than superficially. Halogen salts of calcium and magnesia behave similarly.

Alkali carbonates dissolve aluminium almost as readily as alkali hydroxides; hydrogen is liberated and an alkali aluminate and a hydrogen carbonate are formed. Ammonia solution, concentrated or dilute, also attacks the metal so long as the aluminate dissolves in the excess of alkali, but the action ceases when a film of the aluminate begins to form on the metal.

It follows generally that aluminium is much more liable to be attacked than is commonly supposed, and is unsuitable for the construction of cooking utensils and the like. C. H. B.

**Preparation of Cobaltammine Salt.** By SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1898, 19, 78—80).—The hexammine chloride always contains a small quantity of chloropentammine chloride. This is easily removed by recrystallisation from a small quantity of 5 per cent. ammonia, when it is converted into basic aquopentammine chloride which remains in the mother liquors.

Chloropentammine chloride, which, when prepared by the ordinary methods, always contains a small quantity of the hexammine chloride, cannot be separated from this compound by recrystallisation from dilute hydrochloric acid. It is purified as follows: the crude salt (20 grams) is dissolved in ammonia water (2 per cent. 250 c.c.), the filtrate is mixed with a solution of sodium pyrophosphate (4 per cent. 100 c.c.), and then with concentrated ammonia (700 c.c.) and allowed to remain with occasional stirring. The sodium hexammine pyrophosphate is precipitated, and the aquopentammine salt in the filtrate is converted into chloropentammine chloride by heating with concentrated hydrochloric acid on the water-bath. This reaction affords a good method for the detection of small quantities of the hexammine chloride. The salt (0.2 gram) is dissolved in dilute hydrochloric acid and boiled, and the cold filtered solution treated with a solution of sodium pyrophosphate and ammonia; in the presence of 0.2 per cent. of hexammine chloride, a precipitate is formed after 7 hours; with 2.0 per cent., a precipitate is formed in 2 minutes. E. C. R.

**Chromosulphochromic Acids.** By ALBERT RECOURA (*Bull. Soc. Chim.*, 1897, [iii], 17, 934—938. Compare Abstr., 1893, ii, 470 and 528; 1896, ii, 27, and 1897, ii, 172).—The author has already shown that the green sulphate of chromium forms compounds with one, two and three molecular proportions of sulphuric acid yielding definite salt-forming acids. An analogous series of compounds are obtained by its union with chromic acid; they have the compositions  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{CrO}_4\text{H}_2$ ,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 2\text{CrO}_4\text{H}_2$ , and  $\text{Cr}_2(\text{SO}_4)_3 \cdot 3\text{CrO}_4\text{H}_2$  respectively, and are termed by the author chromosulphochromic acids.

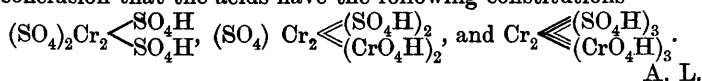
When molecular proportions of green chromium sulphate and potassium chromate are simultaneously dissolved in water, the solution gives no precipitate with barium chloride or silver nitrate; if two molecular proportions of potassium chromate or chromic acid be employed, the same result is obtained, and the product on evaporation

and subjection to a temperature of  $150^{\circ}$  is no longer soluble in water, and the latter statement is also true of the product obtained by using three molecular proportions of chromate. The use of more than three molecular proportions of chromate leads to the formation of a solution which gives a precipitate with silver nitrate, hence the limit of combination has been passed.

In order to isolate the acids, the liquids are evaporated to dryness on the water-bath, when they are obtained in the form of green, amorphous substances, and the salts may be dealt with in a similar manner. In the dissolved state, the substance containing one molecular proportion of chromate is yellowish-green, with two molecular proportions, greenish-brown, and with three molecular proportions, brown; the last form does not appear to be capable of existence in the solid state, as it becomes covered with a yellowish efflorescence due to separation of chromate.

The compounds are very unstable, and are readily resolved into their components; thus a solution recently made is incapable of yielding precipitates with barium or silver salts, but does so after the lapse of 42 hours; moreover, the above statements regarding the action of barium chloride and silver nitrate solutions only hold true when the solutions are very dilute (1/200 mol. of chromate per litre, and 1/10 mol. of barium chloride or silver nitrate per litre), and in no case does the addition of a solution of lead nitrate fail to produce precipitation.

The study of the heat of neutralisation of the new acids has led to the conclusion that the acids have the following constitutions



**Preparation and Properties of Thorium Carbide.** By HENRI MOISSAN and ALEXANDRE ÉTARD (*Ann. Chim. Phys.*, 1897, [vii], 12, 427—432).—Thoria, when heated in the electric furnace with a sufficient quantity of sugar carbon, yields a crystalline carbide (compare Abstr., 1896, ii, 422); when less carbon is employed, a fused mass is produced, consisting of an alloy of thorium and thorium carbide, which is decomposed by water, yielding acetylene, ethylene and its homologues, methane, and hydrogen. The gases evolved from the crystalline carbide consist chiefly of acetylene and methane, whilst hydrogen predominates in the mixture obtained from the above alloy.

G. T. M.

**Bismuth Suboxide.** By R. SCHNEIDER (*J. pr. Chem.*, 1898, [ii], 58, 562—576).—A severe criticism of Vanino and Treubert's papers (Abstr., 1898, ii, 435, 598); the author upholds the existence of a bismuth suboxide,  $\text{BiO}$ , prepared long ago by himself (*Ann. Phys. Chem.*, 1853, 83, 45) and by others. Vanino and Treubert did not obtain this, but metallic bismuth, or a mixture  $\text{Bi} + \text{Bi}_2\text{O}_3$  instead, because they did not use 1 mol. only of alkaline stannous chloride, and keep the bismuth solution (1 mol.) always in excess, but added the latter gradually to 3 mols. of the stannous solution. Under these circumstances, the

bismuth salt would be completely reduced to the metal, and even in the presence of 1 mol. only of the stannous compound the first third added would be so reduced, in which reaction all the stannous compound would be oxidised to the stannic state, so that the remaining two-thirds of the bismuth salt would be precipitated by the alkali present as the oxide, or, rather, the hydroxide. C. F. B.

**Catalytic Action of Platinum and Palladium Sponge.** By ALEXANDER DE HEMPTINNE (*Chem. Centr.*, 1898, ii, 884—885; from *Bull. Acad. roy. Belg.*, [iii], 36, 155—172).—If the catalytic action of platinum is due to its power of condensing gases, then at lower temperatures it should absorb larger quantities of gas; the author finds, however, that platinum sponge absorbs far less hydrogen at  $-78^{\circ}$  than at  $15^{\circ}$ , whilst carbon at  $-78^{\circ}$  absorbs six times as much hydrogen as it does at  $15^{\circ}$ . Moreover, at the temperature of liquid air (about  $-190^{\circ}$ ), platinum sponge still brings about the combination of oxygen and hydrogen, whilst at this temperature even sodium has no action on sulphuric acid. Platinum also absorbs less carbonic oxide at  $-78^{\circ}$  than at  $15^{\circ}$ , but as the difference is less in this case than in the case of hydrogen, the absorption of the gas cannot be due to porosity, since the effect of low temperatures would be a greater diminution in the case of carbonic oxide, owing to its larger molecules, than in the case of hydrogen. Palladium behaves towards hydrogen and carbonic oxide in a similar way to platinum; the author found that when palladium which had been exposed to carbonic oxide was cooled to  $-78^{\circ}$ , then placed in hydrogen, and the temperature allowed to rise, a sudden absorption of gas took place at  $20^{\circ}$ . This remarkable behaviour of palladium is rather in support of the occlusion hypothesis.

E. W. W.

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## Mineralogical Chemistry.

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Cause of the Absence of Colour in Certain Limpid Natural Waters. By WALTHER SPRING (*Rec. Trav. Chim.*, 1898, 17, 359—375. Compare Abstr., 1884, 259, and *Bull. Acad. roy. Belg.*, 1886, [iii], 12, 814, and 1897, [iii], 34, 578).—Although it is well recognised that pure water is blue when viewed through a thickness greater than 1 metre, the only natural waters which appear blue are those of mountain streams which have their origin in the ice and snow of great altitudes. Berzelius has stated (*Jabresbericht*, 1830, 9, 207) that the extraordinarily clear water of Lake Wettern, in Sweden, is perfectly colourless when viewed through a thickness of more than 32 feet, and has hence raised objection to the view that pure water is blue. The author has previously shown (*loc. cit.*) that if water contains one ten-millionth part of its weight of colloidal ferrichydroxide, it no longer appears blue, but green in colour; with quantities greater than this, the colour is yellow or brown. By macerating fragments of

a red rock, such as a Devonian schist, during several weeks with frequently renewed hot caustic potash, and subsequently washing with water by repeated decantation, a point is ultimately reached when the red coloring-matter ceases to subside from the washing water, even after standing several months; the particles of suspended ferric oxide (hæmatite) are no longer visible under a magnifying power of 150 diameters, and probably correspond with the dust of the Devonian epoch. On adding a few drops of this turbid solution to a large volume of pure water, the latter is rendered perfectly clear and colourless when viewed through a thickness of 6 metres. When the proportion of ferric oxide, however, is increased, the water quenches more and more of the transmitted light, until it finally becomes opaque, although appearing red by reflected light.

These observations explain the fact that terrestrial waters rarely appear blue. That the waters of Alpine streams are generally blue is probably due to their being entirely free from suspended anhydrous ferric oxide; the cosmic dust with which they are often contaminated consists principally of meteoric iron, which possesses different optical properties from hæmatite, and is incapable of destroying the natural blue colour of the water. W. A. D.

**Mud Volcanoes of Achtala.** By PETR G. MELIKOFF (*Zeit. anorg. Chem.*, 1898, 19, 1—10).—The author has examined the mud thrown up by these volcanoes; it has a temperature of 22°, and when allowed to settle yields an opalescent liquid which can be rendered clear by filtration. This liquid has the sp. gr. = 1·015 at 17·5° and contains SiO<sub>2</sub>, 0·0018; SO<sub>3</sub>, 0·00203; CO<sub>2</sub>, 0·0889; Cl, 0·0676; Br, 0·00583; I, 0·001356; CaO, 0·0035; MgO, 0·0118; Na, 0·76026; K, 0·01518; Li, 0·00014 per cent., with a small quantity of organic acids.

The author discusses the formation of the sodium carbonate, and shows that it can be formed by the action of calcium carbonate in the presence of carbonic acid on sodium sulphate or chloride, especially in the presence of colloidal substances like iron or aluminium hydroxides.

The mud from the volcanoes contains 83·68 per cent. of clay (diameter of particles 0·005 mm.) containing amorphous silica and crystals of calcite, orthoclase, and quartz; the coarser portion consists of quartz, orthoclase, sanidine, hornblende, bronzite, and magnetite. The clay also contains 0·008 per cent. of ammonia and amine bases.

E. C. R.

**The Black Phosphates of the Pyrenees.** By DAVID LEVAT (*Compt. rend.*, 1898, 127, 834—836).—The author finds that between the upper Devonian marble or "*griotte*" of the Pyrenees and the subjacent schists, there extends a continuous stratum of black material which varies in thickness from 8 to 10 metres, and closely resembles anthracite in appearance; it appears to extend from Oloron, Basses-Pyrénées, throughout the whole length of the mountain chain into Herault, and consists largely of tricalcium phosphate. This formation, which has been mentioned by other observers under the names *black schists*, *carbonaceous schists*, *impure anthracite*, and *graphitic stratum* (*couche graphiteuse*), is characterised by there being imbedded

in it black, imbricated nodules, which form a quarter to a third of its total mass, and contain from 65—75 per cent. of tricalcium phosphate. The matrix, after removing the nodules, contains from 14—16 per cent. of phosphoric acid; the dull schistose material resembling slate, which is present in the stratum, contains 7.1 per cent. of the same acid, whilst the lustrous schists which envelop the nodules contain 11.7 per cent. The black phosphates are usually impregnated with organic matter, in some cases to the extent of 28 per cent.; the nitrogen present varies from 0.3—0.5 per cent. W. A. D.

**Meteorite from Migheja.** By PETR G. MELIKOFF and W. KRSCHISCHANOWSKY (*Zeit. anorg. Chem.*, 1898, 19, 11—17).—This meteorite fell on June 9th, 1889. It is a somewhat porous mass permeated with amorphous carbon, gives a black streak on paper, and when rubbed a characteristic odour which resembles that of a bituminous substance. Analysis gave,

SiO <sub>2</sub> .	CaO.	MgO.	FeO.	MnO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> .	FeS.
27.49	2.11	19.85	26.95	0.65	1.37	0.17	1.62	0.46
NiFe <sub>3</sub> .	Chromite.	P.	S.	SO <sub>3</sub>	S <sub>2</sub> O <sub>3</sub> .	C.	H <sub>2</sub> O	
3.95	1.62	0.15	3.10	0.85	0.12	2.63	1.40	

It contains free sulphur and metallic sulphates, sulphites, and thiosulphites. The free metals are not completely soluble in mercuric chloride. The soluble silicate consists for the most part of olivine of the composition  $3(\text{MgO})_2\text{SiO}_2, 2(\text{FeO})_2\text{SiO}_2$ . The insoluble silicate is a disilicate of the pyroxene group. E. C. R.

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## Physiological Chemistry.

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**Absorption of Proteids.** By LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1899, 2, 137—141).—By feeding dogs on moderate quantities of a soluble proteid (Witte's peptone), the old view, namely, that proteid is chiefly absorbed by the capillaries of the villi is confirmed. Asher and Barbera's work, which advanced the view that lymph is due to increased glandular activity and acts as an important channel for proteid absorption, is criticised. W. D. H.

**The Basic and Acid Capacity of the Blood and of Proteids.** By KARL SPIRO and WILHELM PEMSEL (*Zeit physiol. Chem.*, 1898, 26, 233—271).—The observations, made principally on the blood and serum of the horse, show that these fluids have different acid and basic capacities. By different methods, three values for the alkalinity of the blood were obtained; one corresponds with numbers given by Löwy, and represents the alkalinity of the carbonates and phosphates of the serum (diffusible alkali). The second value is higher, and represents the additional alkalinity due to proteids which unite with alkali (Jaquet's sub-acid substances); this disappears when the proteids are 'salted out' with ammonium sulphate. The third value takes into

account the acid capacity of the blood, which is principally a property of the corpuscles. The proteids themselves are hardly considered to function either as acids or bases, for although they are electrically charged, they are not ionised.

W. D. H.

**Influence of Copper and Zinc Salts on Hæmoglobin Formation.** By W. WOLF (*Zeit. physiol. Chem.*, 1899, 26, 442—461).—Some authors have stated that copper and zinc salts are favourable to hæmoglobin formation, but the present experiments on rats do not confirm this, the amount of hæmoglobin and of red corpuscles being practically the same as in control animals.

W. D. H.

**Oxyhæmoglobin of the Horse.** By D. LAWROFF (*Zeit. physiol. Chem.*, 1898, 26, 343—349).—Horse's oxyhæmoglobin yields 94·09 of proteid, 4·47 of hæmatin, and 1·44 per cent. of other substances; these numbers are rather different from those of Schulz (*Zeit. physiol. Chem.*, 24, 449), who gives proteid, 86·5; hæmatin, 4·2, and other constituents, 9·2 per cent. The proteid material, globin, is regarded as one *sui generis*; the other materials have not yet been fully investigated, but they yield fatty acids and ammonia.

W. D. H.

**Iron in Blood-plasma and Leucocytes.** By EMIL HÄUSERMANN (*Zeit. physiol. Chem.*, 1899, 26, 436—437).—Blood was prevented from coagulating by sodium fluoride, and the corpuscles separated from the plasma by the centrifuge. The plasma contains from 1 to 7 milligrams of iron per 100 grams, probably derived from the disintegration of leucocytes; fibrin contains from 9 to 10 milligrams of iron per 100 grams.

W. D. H.

**Paraglobulin of Blood-serum.** By PROSPER VAN DE KERCKHOF (*Chem. Centr.*, 1898, ii, 494; from *Bull. Acad. roy. Belg.*, [iii], 35, 562—567).—The author has prepared paraglobulin from the blood-serum of oxen, sheep, swine, and dogs, partly by salting out with magnesium sulphate, and partly by half-saturating with ammonium sulphate. After fractionally coagulating, the paraglobulin obtained from mammals appears to consist of three or four different kinds, distinguished by different temperatures of coagulation and different rotatory powers; one kind is not precipitated by sodium chloride.

E. W. W.

**The Suprarenal Capsules.** By GEORGE P. DREYER (*Amer. J. Physiol.*, 1899, 2, 203—219).—The active principle of suprarenal extract is present in the blood of the suprarenal vein, and, therefore, constitutes a true internal secretion. This conclusion is based upon the result (rise of arterial blood pressure) which follows the injection of this blood derived from one dog into the circulation of another; there is no chemical analysis recorded to support the contention. The amount of this substance (again judged by the physiological effect of injection) is increased by electrical stimulation of the splanchnic nerve below the diaphragm, and this nerve is, therefore, regarded as containing the secretory fibres for the gland. The increased secretion is independent of the vascular changes simultaneously provoked.

W. D. H.



**Chemistry of the Thyroid.** By ERNST ROOS (*Zeit. physiol. Chem.*, 1899, 26, 429—435).—Polemical. Critical remarks on the paper recently published by Blum (this vol., ii, 160). W. D. H.

**The Microchemical Detection [Localisation] of Phosphorus in Animal and Vegetable Tissues.** By A. B. MACALLUM (*Proc. Roy. Soc.*, 1898, 63, 467—479).—The localisation of phosphorus in the tissue elements by microchemical means is a question of considerable importance, but the method introduced by Lilienfeld and Monti for the purpose (*Abstr.*, 1893, ii, 135) is fallacious. The following new method is recommended. Sections of fresh tissues, after treatment with alcohol, are placed in nitromolybdate for times varying from 10 minutes to 48 hours, at 35°. The inorganic phosphates are first affected, then lecithin, then the phosphorus combined in nuclein and similar substances; the lecithin may, however, be previously removed with boiling alcohol. The sections are then placed in a reducing solution, the best for the purpose being a 1 to 4 per cent. solution of phenylhydrazine hydrochloride; this brings out a green colour where the phosphomolybdate compound occurs, but only a faint yellow reaction when ammonium molybdate alone is present. The preparations are then dehydrated, cleared, and mounted in the usual way. The results obtained with various animal and vegetable tissues are described. W. D. H.

**Relation between the Growth of the Progeny and Composition of the Milk, and between the Ash of the Progeny and that of the Milk.** By EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1899, 26, 487—497; 498—500).—The experiments were made on rabbits, cats, and dogs; numerous analytical details are given, and the results on the whole confirm Bunge's well-known views on the subject. W. D. H.

**Freezing Point of Milk.** By JUSTIN WINTER (*Bull. Soc. Chim.*, [iii], 17, 999—1003. Compare *Abstr.*, 1896, ii, 199; 1897, ii, 112 and 378).—A controversial paper in which the author reaffirms the statement that milk has a constant freezing point. T. M. L.

**A New Proteid Constituent of Milk.** By AUGUSTIN WRÓBLEWSKI (*Zeit. physiol. Chem.*, 1898, 26, 308—313).—A new proteid material is obtainable from milk by 'salting out' with sodium chloride, after the caseinogen has been precipitated with acetic acid. Its percentage composition is C, 45.01; H, 7.31; N, 15.07; P, 0.8; S, 4.7, and O, 27.11. After boiling with sulphuric acid, it reduces Fehling's solution; by peptic digestion, it yields no pseudonuclein; as it is neither coagulated by heat, nor precipitated by dialysis, it is neither albumin nor globulin. On account of the opalescent character of its solutions, the name *opalisin* is given to it. It is abundant in human milk, less abundant in mare's milk, and scanty in cow's milk. It is the presence of this proteid which makes the precipitation of the casein of human milk so difficult. W. D. H.

**The Sugar of Diabetic Urine.** By LE GOFF (*Compt. rend.*, 1898, 127, 817—819).—See this vol., i, 242.

**Alloxuric Bases Present in Urine.** By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1898, 26, 350—380. Compare Abstr., 1895, ii, 94; 1896, ii, 200; and 1898, i, 699).—The authors now employ a different method for separating the alloxuric bases in human urine, which consists in precipitating the alloxuric compounds with ammoniacal silver solution, or with copper sulphate and sodium hydrogen sulphite, decomposing their silver or cuprous derivatives with hydrochloric acid or with hydrogen sulphide in presence of this acid, evaporating to dryness the filtrate from the inorganic precipitate, and digesting the residue with warm water; the insoluble portion now consists of the xanthine fraction, whilst the solution contains the hypoxanthine fraction, together with paraxanthine. The insoluble portion is dissolved in dilute soda, and the heteroxanthine separated by means of its sodium derivative; the solution acidified with moderately strong nitric acid yields xanthine nitrate; from the final filtrate, 1-methylxanthine is precipitated on the addition of ammonia.

On methylation, 1-methylxanthine yields successively theophylline and caffeine. *Bromo-1-methylxanthine*, produced by heating the base with excess of bromine at 110° for 6 hours, is obtained in aggregates of pyramids; it is not decomposed on heating to 295°.

Epiguanine is precipitated from the solution of the hypoxanthine fraction on adding ammonia; the filtrate, freed from excess of this reagent and treated with a solution of picric acid, yields adenine picrate. The bases still remaining in solution are precipitated in the form of their silver or cuprous derivatives, and the latter compounds are decomposed by hydrogen sulphide; the filtrate from the metallic sulphide, when evaporated to a small bulk and acidified with nitric acid, yields hypoxanthine nitrate. The mother liquor contains, besides paraxanthine, a certain quantity of heteroxanthine, 1-methylxanthine, and hypoxanthine, and the whole process is repeated on this fraction; from the final filtrates, paraxanthine is obtained, either as the free base or as the sodium derivative. Guanine and carnine are not found in either of the above fractions.

The authors now find that the following quantities of alloxuric bases are contained in 10,000 litres of human urine: 10·11 grams of xanthine, 22·345 grams of heteroxanthine, 31·285 grams of 1-methylxanthine, 15·31 grams of paraxanthine, 8·50 grams of hypoxanthine, 3·54 grams of adenine, and 3·40 grams of epiguanine. The bases adenine, hypoxanthine, and xanthine, due to the breaking down of nuclein, occur in smaller quantities than the homologues of xanthine, which are probably derived from the theobromine, caffeine, and theophylline introduced into the system by the use of tea and coffee, paraxanthine (1:7-dimethylxanthine) being obtained from caffeine (1:3:7-trimethylxanthine), heteroxanthine (7-methylxanthine) from theobromine (3:7-dimethylxanthine), and 1-methylxanthine from theophylline (1:3-dimethylxanthine) by the elimination of the labile methyl group in position 3. (Compare Abstr., 1895, i, 434.) G. T. M.

**Physiological Action of Certain Derivatives of Proteids.** By RUSSELL H. CHITTENDEN, LAFAYETTE B. MENDEL, and YANDELL HENDERSON (*Amer. J. Physiol.*, 1899, 2, 142—181).—The substances

investigated are various forms of albumose and peptone prepared from proteid and gelatin; the anti-albumose used was made by digesting anti-albumid. The injection of such substances into the blood stream causes a slight initial rise of arterial blood pressure, due to the momentary increase of the vascular contents; this is followed by a fall. The gelatin products cause a very small effect; so also do anti-albumid, and especially anti-peptone. The albumoses act vigorously, especially heteroalbumose.

The effect of hindering blood-coagulation does not run parallel to the preceding; the two phenomena are, therefore, independent; the order of activity in retarding coagulation is albumose, anti-albumid, peptone. Protogelatose hastens coagulation; large doses of deuterogelatose retard it; gelatin-peptone accelerates it slightly.

Experiments on immunity partly confirm Grosjean's observations, and extend them by showing that the immunity acquired to subsequent injections is by no means characteristic of the specific products injected, but due to a specific reaction produced in each case within the organism itself.

Anti-albumid, hemipeptone heteroalbumose, and deuterogelatose act as true lymphagogues. The anti-clotting substance is probably formed in the liver, and reaches the blood mainly through the lymph.

Most of the substances injected lessen the flow of urine; this is specially the case with heteroalbumose, even though the fall of blood-pressure it causes may not be marked. Anti-albumid appears to act specifically also on the kidneys, although in a less degree. Large doses of hemipeptones and the gelatoses may act as diuretics; when this occurs, the primary proteoses undergo hydrolysis, and pass into the urine as deuteroproteose.

The paper concludes with theoretical remarks on proteolytic products in view of recent work which appears to upset the old idea of Kühne on the subdivision of these products into hemi- and anti-groups.

W. D. H.

**Fat in the Liver of Infants Suffering from Gastro-Enteritis.** By MARTIN THIEMICH (*Zeit. physiol. Chem.*, 1898, 26, 189—217).—From observations on cases of gastro-enteritis in infants, some of which showed fatty livers, the conclusion is drawn that the hepatic condition is due rather to fatty infiltration than to fatty degeneration. The composition of the liver fat is markedly different from that of the fat in the food (milk); moreover, absorption of fat from the alimentary canal is at a minimum. The fat is considered to be derived from the subcutaneous tissues, but there is not a complete agreement in the composition of the fat from the two sources, the fat from the liver being richer in oleic acid, and poorer in the solid fatty acids.

W. D. H.

**Antagonism Between Toxins and Antitoxins.** By CHARLES JAMES MARTIN and THOMAS CHERRY (*Proc. Roy. Soc.*, 1898, 63, 420—432).—Behring maintains that the antagonism between toxins and antitoxins is a chemical one, whilst Buchner and others consider that the interaction takes place only through the intervention of the cells of the organism. The present paper describes experiments which

strongly support the former view. The toxins and antitoxins used were those of snake venom and of diphtheria. The principal experiments which support the second view are those of Calmette, who found that cobra poison is not destroyed by heating its solutions to  $68^{\circ}$  for 10 minutes, but that antitoxin is completely destroyed; a mixture of the venom and antivenin produces no symptoms when injected into animals, but if the two substances had remained in contact for 10 minutes, and were then heated to  $68^{\circ}$  for 10 minutes before injection, death ensued. He therefore concludes that the two substances do not interact *in vitro*.

The present experiments show that the fact recorded by Calmette is quite true, but if the two substances remain in contact for more than 10 minutes in the test-tube, the interaction does take place, and subsequent injection after heating is innocuous. Calmette did not sufficiently heed the value of the factor time; in the case of heavy molecules like those of toxin and antitoxin, the velocity coefficient is a high one.

From experiments on filtration through gelatin films, the conclusion is drawn that the antitoxin molecule is the heavier of the two; it will not pass through a gelatin filter, whereas the toxin will. This confirms previous experiments made by Brodie; the toxin is an albumose, the antitoxin a globulin, or at least their molecules stand on about the same level. In a mixture of the two substances, the toxin can be separated by the use of such a filter, but if the two substances are allowed to remain in contact for a sufficient time before filtration, the filtrate is free from toxin. The proof that the two substances do neutralise each other *in vitro* is thus most complete. W. D. H.

**Analogies between the Physiological Effects of High Temperature, Lack of Oxygen, and Certain Poisons.** By WILLIAM D. ZOETHOUT (*Amer. J. Physiol.*, 1899, 2, 220—242).—Alkalis in very small percentage ( $\frac{1}{100}$ — $\frac{1}{2000}$  per cent.) increase the resistance of *Paramœcia* to heat ( $36$ — $40^{\circ}$ ), to the lack of oxygen, and to the destructive action of potassium cyanide and atropine. Acids on the other hand, never increase, but when at all active always decrease the power of resistance to the agents named. The explanation advanced is that the lack of oxygen (produced by hydrogen atmosphere, or by poisons preventing oxidation) and high temperature cause the formation of certain substances which render the transformation of chemical into molecular energy impossible, thereby producing death. These substances are in some way antagonised by alkalis but not by acids. W. D. H.

**Acetonuria in Phloridzin Poisoning.** By H. CHR. GEELMUYDEN (*Zeit. physiol. Chem.*, 1898, 26, 381—389).—In starving dogs, phloridzin causes both glycosuria and acetonuria, but the acetonuria is insignificant if the animal has been fed on food containing proteids or carbohydrates, a carbohydrate diet especially hindering acetonuria, but with very large doses of phloridzin, acetonuria appears, in spite of the diet. Two experiments on fat-feeding showed in one case a disappearance of the acetonuria, in the other an increase. Butyric

acid, in doses of 2 grams, given by the stomach, increases the acetonuria, but when it is subcutaneously injected, the effect is very slight. Butyric acid has not this effect if phloridzin is not given as well.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Alcoholic Fermentation without Yeast Cells.** VIII. By EDUARD BUCHNER and RUDOLF RAPP (*Ber.*, 1899, 32, 127—137. Compare Abstr., 1897, ii, 154 and 380, and 1898, ii, 127, 246, 346, 396, and 480).—In order to ascertain whether the fermenting action of yeast-extract is due to a soluble enzyme or to particles of living protoplasm, the authors have made use of a centrifugal machine, and find that, after 2 to 5 hours, no difference can be detected in the fermenting power of the upper and lower layers of the extract. They also show that the fermentation is not hindered by the addition of large quantities of glycerol to the extract. Although this would suffice to kill any living organisms that might be present, the fermenting power of yeast cells under similar conditions was found to agree closely with that of the extract when the quantity taken was such as would contain an equal weight of nitrogen. Desiccated yeast-extract was found to be unaltered after 2 months, but had a lower fermenting power when kept for 7 or 8 months; it was not changed by heating at 85° for 8 hours, but its action on cane sugar was almost entirely destroyed by heating at 97° during 6 hours.

The latter part of the paper is in answer to Abeles (Abstr., 1898, ii, 621), who regards the fermentation as due to living protoplasm in the extract.

T. M. L.

**Formation of Glycogen in Yeast.** By E. KAYSER and E. BOULLANGER (*Chem. Centr.*, 1898, ii, 440—441; from *Ann. Brass. et Dist.*, 1898).—The authors have cultivated wine-yeast in solutions of cane- or grape-sugar and then determined the amount of glycogen formed, by counting the number of cells which are coloured reddish-brown or yellow by iodine solution. Both kinds of sugar appear to yield glycogen with equal facility. In weak sugar solutions, the glycogen disappears quickly, whilst solutions containing 10—15 per cent. of sugar do not suffer loss even on long exposure to the air. When cultivations are made in open dishes, less glycogen is formed, and it disappears more quickly, especially in weak solutions, than when the surface exposed to the air is limited by employing narrow tubes. With a 20 per cent. solution, the glycogen is formed very slowly, as at first the cells only multiply very gradually, but after a time 80 per cent. of the cells give a reddish-brown coloration with iodine.

The authors have also determined the influence of tartaric, malic, and citric acids on the production of glycogen; the smaller the quantity of acid present, the greater the quantity of glycogen formed

and the more slowly it disappears. Tartaric acid is the most effective in preventing the formation of glycogen, but the nature of the yeast and the temperature of the fermentation have a great influence. Acetic acid does not exert any preventive action, and acts like alcohol in preserving the glycogen, the yeast possibly deriving its nutriment from the acid on converting it into glycogen. When peptone is used in the cultivations, less volatile acids are formed, and the glycogen appears and disappears more quickly. The formation of glycogen also depends on the amount of sugar present, the temperature, the quantity of nitrogen in the nutritive material, and on the conditions of access to the air.

E. W. W.

**Chemistry of Tubercle Bacilli.** By W. G. RUPPEL (*Zeit. physiol. Chem.*, 1898, 26, 218—232).—About 18 to 20 per cent. of the tubercle bacilli (obtained in mass, and extracted by methods given in full detail) consists of proteose-like substances, in the main analogous to the atmid-albumoses of Neumeister. There is also an insoluble substance, which is often abundant, and appears to be characteristic, and probably is the active substance in tuberculin. It contains 9.42 per cent. of phosphorus; its exact nature is at present uncertain. The name 'tuberculic acid' is suggested.

W. D. H.

**Assimilation of Oxidised and Amidic Nitrogen by the Higher Plants.** By MAZÉ (*Compt. rend.*, 1898, 127, 1031—1033).—A series of comparative experiments, made on the relative influence of nitrates and ammonium salts, on the germination of the seeds of maize, bean, and vetch plants in sterilised nutritive solutions, and in aqueous solutions containing only the nitrogenous salts, indicate that ammonium sulphate and sodium nitrate are equally favourable to the growth of the plant, and that ammonia is absorbed as such, for no trace of nitrates or nitrites could be detected in the solutions containing the ammonium salt at the conclusion of the experiment.

G. T. M.

**Nitrogen Nutrition of Plants.** By L. RICHTER (*Landw. Versuchs-Stat.*, 1898, 51, 220—241).—Peas, buckwheat, oats, and mustard were grown in pots containing a mixture of sand (3600) and soil (1200 grams) containing 4.584 grams of nitrogen per pot. There were 15 pots to each plant, and the conditions were as follows. A, (pots 1—4) not sterilised and inoculated; B.a, (5—8) sterilised and inoculated; B.b, sterilised, inoculated, and again sterilised after each crop; B.c, same as B.b, but not inoculated. From pots 4, 8, and 15, one crop was obtained; from pots 7, 11, and 14, two crops, and from the rest, three crops in the same season. Pots 1, 5, and 9 received 0.5 gram of nitrogen as nitrate after the first and second crops.

The peas alone were able to utilise the free nitrogen of the air and give good second and third crops, whilst the produce of the other plants diminished as the supply of nitrogen in the soil became less. In each case, the soil which was not sterilised, and which received no nitrate, showed a gain of nitrogen; where nitrate was added, there was a loss of nitrogen in the soil. Nitrogen fixation in the soil seems, therefore, only to take place when the amount of assimilable nitrogen begins to fail. Most of the sterilised pots showed a loss of nitrogen,

due, probably, to the manurial effect of the available nitrogen liberated in the process of sterilising by heat.

In 1895, similar experiments were made with oats. In addition to the nitrate pots, there were also pots manured with the same amount of nitrogen in the form of asparagine. The results confirmed those previously obtained: gain of nitrogen in unsterilised soil in which the available nitrogen has been used up; loss of nitrogen in presence of readily assimilable nitrogen compounds. The loss in fallow pots manured with asparagine was, however, very slight as compared with the nitrate pots. There is no conclusive evidence to show whether the loss of nitrogen is due to micro-organisms. The losses of nitrogen in the sterilised pots diminished towards the end of the experiment, and in some cases there was finally a gain; this is explained on the assumption that the available nitrogen became exhausted and the soil was thus reduced to the condition in which fixation of nitrogen takes place.

N. H. J. M.

**Selective Absorption of Certain Elements by Plants.** By E. DEMOUSSY (*Compt. rend.*, 1898, 127, 970—972. Compare *ibid.*, 771).—In the experiments now described, the plants were grown in different solutions, each containing two salts. *Potassium nitrate and chloride.*—Buckwheat was grown in a solution containing  $1\frac{1}{2}$  mols. of each salt in milligrams per 100 c.c. After 5 days, the analysis of the solution showed that 6.5 milligrams of nitric acid and only 2.7 milligrams of chlorine had been absorbed, that is to say, 31 per cent. of the nitrogen and 5 per cent. of the chlorine had been assimilated. Colza gave similar results. *Potassium and calcium.*—In a solution containing K, 84, and Ca, 42 milligrams, wheat absorbed in 4 days, K, 57.4, and Ca, 13 milligrams, or 68.3 and 30.7 per cent. respectively. Similar results were obtained with rye, peas, colza, and lentils. *Sodium and calcium.*—Colza absorbed rather less calcium than sodium, maize rather more. *Potassium and sodium.*—Colza absorbed 40 milligrams of potassium, but no sodium; rye absorbed a very small amount of sodium, and 22 times as much potassium. In presence of potassium, the absorption of sodium is greatly diminished, or even completely prevented.

In the case of solutions containing one substance, the substance is absorbed by the plant if not injurious, but certain injurious substances are absorbed only in small amounts. With complex solutions, the plant exercises a selective power.

In all the experiments, very young plants were employed.

N. H. J. M.

**Researches on the Vegetation of Certain Algæ.** By RAOUL BOUILHAC (*Ann. Agron.*, 1898, 24, 561—602).—The investigation included (1) effect of arsenic acid on the growth of algæ, (2) fixation of atmospheric nitrogen by bacteria associated with algæ, and (3) cultivation of green algæ in presence of organic matter, both with and without access of light. Many algæ were found to vegetate in solutions containing potassium arsenite; some are benefited by it, and in some cases arsenates may partially take the place of phosphates.

*Schizothrix lardacea*, *Ulothrix flaccida*, and *Nostoc punctiforme* are alone unable to develop in non-nitrogenous solutions. In presence of



soil bacteria, however, *Nostoc* utilises atmospheric nitrogen and develops normally. On exposure to light, normal growth, accompanied by fixation of nitrogen, is obtained in entire absence of organic matter. In dilute solutions of glucose, *Nostoc* grows rapidly when soil bacteria are present, the yield being increased fourfold as compared with the growth obtained in purely mineral solutions.

Without, or with, insufficient light, *Nostoc* only grows in presence of organic matter such as glucose. With a temperature of 30°, it may be grown in glucose solutions in absolute darkness, retaining its green colour; the green colouring matter was shown by its spectrum to be chlorophyll (compare this vol., ii, 46). The amount of glucose must not exceed 1 per cent., as *Nostoc* is unable to live in stronger solutions.

N. H. J. M.

**Influence of Anæsthetics on the Formation of Chlorophyll by Plants.** By E. C. TÉODORESCO and HENRI COUPIN (*Compt. rend.*, 1898, 127, 884—887).—Bernard suggested that anæsthetics influence plants by preventing the assimilation of carbon; the authors now find that chloroform and ether prevent the formation of chlorophyll in etiolated plants exposed to diffused sunlight. In the experiments described, the anæsthetic (0·8—5·5 c.c.) was vaporised beneath glass shades which were sufficiently large not to interfere with the respiratory exchange of gases of the plants grown beneath them; the influence of the anæsthetic was determined by comparing the plants with those grown in the open air under conditions otherwise similar. The plants studied were wheat, vetch, white lupin, and buckwheat, and the formation of chlorophyll was observed during periods ranging from 5 to 24 hours. The quantity of the same anæsthetic necessary to produce the maximum retardation in the production of chlorophyll varies, although between somewhat narrow limits, for different plants; if an excess be employed, the plant sickens and dies. If less of the anæsthetic be employed than that corresponding with complete cessation of chlorophyll formation, the etiolated plants slowly become green, although marked retardation in comparison with the control plants is observed.

W. A. D.

**Digestion of Starch in Plants.** By LECLERC DU SABLON (*Compt. rend.*, 1898, 127, 968—970).—The author has investigated the digestion of starch in certain bulbs and tubers by the diastases present in the plants themselves during the digestion of the reserve materials. With a view to accelerate this action, the organs were in some cases crushed in presence of water and the increased rate of digestion observed. In this way, he has found that in the lily, tulip, hyacinth, arum, fœcœ, and colchicum the starch is converted into dextrin, and as digestion proceeds a sugar is formed that seems to be a saccharose with a lower reducing power than maltose, and may be different in different plants. At a still later stage, part at least of the sugar is converted into glucose. In the onion and the asphodel, the saccharose is gradually converted into glucose. It follows that the diastatic digestion of starch in living plants does not stop at the formation of a saccharose, but continues until the starch has been directly converted into assimilable glucose.

C. H. B.

**Decomposition of Proteids in Plants.** By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1899, 26, 411—426. Compare Abstr., 1898, ii, 481).—The research amplifies the author's previous statements as to the importance of the formation of asparagine and glutamine in plants. W. D. H.

**Nitrogenous Materials in Fungi.** By ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1899, 26, 438—441).—Fungi differ from flowering plants in several chemical points. Among the nitrogenous compounds present are large amounts of proteid; leucine and tyrosine were also isolated in a crystalline state. W. D. H.

**An Active Principle in Millet Hay.** By E. F. LADD (*Amer. Chem. J.*, 1898, 20, 861—866).—The exclusive feeding of horses on millet hay (*Setaria Italica*) causes a diseased condition, characterised by a very much increased urination. On macerating well-pulverised millet with alcohol during 8 days, 6.25 per cent. of organic matter is extracted; on evaporating the extract and dissolving the residue in water, a bitter solution is formed which gives no precipitate with copper acetate, and is, therefore, free from tannins. On acidifying the solution, and subsequently extracting with benzene and evaporating, a pale yellow liquid is obtained which solidifies when cooled below the ordinary temperature; it becomes brown on adding concentrated sulphuric acid, yellow in presence of nitric acid, and gives a green precipitate with Frohde's reagent. With phenol, it produces a reddish-brown coloration, and with cane sugar and sulphuric acid, a violet, whilst with lead acetate solution a white precipitate is formed. Although not acted on by alkalis, it is decomposed by sulphuric acid, yielding a sugar which reduces Fehling's solution; it thus appears to consist of a glucoside, and in some respects resembles daphnin. Like the latter, it possesses marked physiological action; the aqueous solution, administered to mice and rats, produces stupefaction after 2 hours, accompanied by very frequent urination. Hypodermic injections produce the same effect, but much more rapidly. W. A. D.

**Occurrence of Hydrocyanic Acid in the Prunaceæ.** By A. J. VAN DER VEN (*Chem. Centr.*, 1898, ii, 678; from *Ned. Tijdsch. Pharm.*, 10, 239—241).—The presence of hydrocyanic acid is detected by the formation of Prussian blue when the extract, obtained by treating the plant with a 5 per cent. solution of sodium hydroxide in alcohol, is poured into a mixture of ferric chloride and ferrous sulphate dissolved in water, and hydrochloric acid then added. The branches of *Prunus laurocerasus* contain 0.05 per cent. in the sieve tubes, the young green twigs yielding the most. The tap-root gives a stronger reaction than the rootlets. The acid is distributed over the whole surface of the old leaves, which contain 0.117—0.101 per cent., whilst those of the previous year have a much smaller content. In the youngest leaves, just unfolded, the acid occurs only in isolated groups of cells along the nerves, and the amount sometimes reaches 0.24 per cent. By keeping the plant in the dark, the amount of acid decreases, and in some plants it entirely disappears. E. W. W.

**Estimation of Tannin in the Oak Barks of the Canton of Geneva.** By WILLIAM BOREL and H. W. DE BLONAY (*Chem. Centr.*, 1898, ii, 796—797; from *Arch. Sci. Phys. Nat. Geneva*, [iv], 6, 160—168).—The object of the investigation was to ascertain the influence of age and of the barking process on the yield of tannin in oak-bark.

The barks were obtained from stems of *Quercus pedunculata* grown on a 430 m. high terrace on "glacier clay soil." The samples were all taken by cutting a ring from the tree at 1 m. distance from the bottom. The analyses were performed by the process recommended by Jean, namely, titration with iodine before and after treatment of the infusion with hide powder. The table shows the influence of age on the percentage of tannin.

5	20	25	32	41	50	51 years.
8.40	7.15	6.60	5.35	5.05	5.00	5.90 per cent.

The smaller percentage of tannin contained in barks from old trees is, however, more than compensated for by the superior yield of bark. The barking process does not influence the amount of tannin, but it causes an increase in the yield of bark of from 25—40 per cent.

L. DE K.

**Constituents of the Seeds of *Picea excelsa*.** Products of the Decomposition of the Proteids of the Seeds. By N. RONGGER (*Landw. Versuchs.-Stat.*, 1898, 51, 89—116).—The percentage composition of the seeds was found to be as follows.

Pro- teids.	Nuclein, &c.	Glycer- ides.	Choles- terol.	Lecithin.	N-free subst. soluble. insol.		Crude fibre.	Ash.	Not deter- mined.
15.89	3.23	35.13	(0.06)	0.12	5.43	7.00	25.40	4.74	3.00

The amount given as proteids was obtained by multiplying the nitrogen by 5.5; that given as nuclein (including other undigestible nitrogen compounds) by multiplying the nitrogen by 7.7. Under glycerides, free fatty acids are included. The sugars present are cane sugar and an amorphous sugar; the latter dissolves readily in water, and after being heated with dilute hydrogen chloride, reduces Fehling's solution. It gives the levulose reaction when heated with resorcinol and hydrochloric acid, and when heated with dilute nitric acid yields mucic acid.  $[\alpha]_D = +105.4^\circ$ . The carbohydrate resembles raffinose, but it yielded more mucic acid than the latter, and is, moreover, not crystalline. The seeds do not contain starch.

The proteids of the seeds, when boiled with hydrochloric acid and stannous chloride, yielded 10.3 per cent. of arginine, and, without doubt, other bases; leucine and tyrosine were also found. The production of so great an amount of arginine is of interest as bearing on the fact that considerable quantities of the substance are found in the young plants from the same seeds, the amount produced being four times the maximum amount obtained by Hedin from proteids of various origin. The results indicate that the proteids from different sources must be differently constituted.

N. H. J. M.

**Constituents of the Seeds of *Pinus Cembra*.** By ERNST SCHULZE and N. RONGGER (*Landw. Versuchs.-Stat.*, 1898, 51, 189—204).—The percentage composition of the whole seeds (1), the husks (2), and the kernels (3) is as follows.

	Proteids N × 6.	Glycer- ides, &c.	Choles- terol.	Leci- thin.	Starch.	N-free substance soluble in H <sub>2</sub> O.	Crude fibre.	Ash.	Not deter- mined.
1.	6.54	14.50	0.03	0.37	2.78	6.24	46.00	1.60	22.0
2.	0.84	1.18	—	—	—	98.18		0.80	—
3.	17.24	49.26	—	0.99	7.43	16.84	1.19	3.05	4.0

The large amount of substances not determined in the seeds is due to the fact that the husks form more than 60 per cent. of the whole seed. The ether extract of the husks (given under glycerides) is solid at the ordinary temperature, dissolves readily in hot alcohol, and probably contains only a small amount of glycerides. As regards the kernels, it may be assumed that the non-nitrogenous substances soluble in water consist mainly of carbohydrates (cane sugar, &c.), and that they do not include much organic acids, &c. The ash of the kernels is rich in phosphoric acid.

N. H. J. M.

**Toxicity of Chromium Compounds with respect to Higher Plants.** By HENRI COUPIN (*Compt. rend.*, 1898, 127, 977—978).—Water culture experiments with wheat, in which different amounts of chromium compounds were added to the solutions, gave the following toxic equivalents, the minimum toxic amounts, per cent.

$K_2Cr_2(SO_4)_2$ 1.142	$Cr_2(SO_4)_3$ 0.5	$CrO_3$ 0.00595	$K_2CrO_4$ 0.0625	$K_2Cr_2O_7$ 0.03125	$Na_2CrO_4$ 0.125
	$Na_2Cr_2O_7$ 0.0064	$Am_2CrO_4$ 0.0625	$Am_2Cr_2O_7$ 0.025		

The greatest effect is thus produced by chromium in the form of chromic acid, whether free or combined. Alkali dichromates are distinctly less active than the corresponding chromates.

N. H. J. M.

**Employment of Alinite in the Cultivation of Cereals.** By L. MALPEAUX (*Ann. Agron.*, 1898, 24, 482—490).—Experiments were made in pots holding about 20 litres, two pots being, in each case, inoculated with the preparation containing *Bacillus Ellenbachensis*, known as alinite, and two being without inoculation. The following average amounts (in grams) were obtained.

	Garden soil.				Forest soil.				Sand.			
	Without alinite.		With alinite.		Without alinite.		With alinite.		Without alinite.		With alinite.	
	grain.	straw.	grain.	straw.	grain.	straw.	grain.	straw.	grain.	straw.	grain.	straw.
Wheat	11	28	14	33	8	24	11	27	5	14	5	15
Barley	11	26	14	34	9	18	11	24	6	12	5	12
Oats	12	38	18	44	11	34	13	34	6	18	6	18

There was, therefore, no increased produce in sand inoculated with alinite, but in soil containing plenty of organic matter, inoculation was

beneficial, owing probably to the destruction of the organic matter. Further experiments, in the field, showed no marked effect when alinite was employed; probably the soil already contained nitrogen-fixing bacteria in sufficient quantity.

N. H. J. M.

**Cultivation of Wheat and Oats at Grignon in 1898.** By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1898, 24, 520—534).—Experiments (1) on the influence of the time of sowing the seed on the amount of produce and (2) with varieties of wheat are described. Good yields of wheat were obtained after clover, and the addition of nitrate was without effect. Nitrate was also without effect on wheat after well manured roots or potatoes; nitrate in conjunction with farmyard manure had, on the contrary, a very marked effect. The season was very favourable for dung, but not for nitrate.

The experiments on oats were also with different varieties.

Referring to that portion of Sir W. Crookes' Address to the British Association (1898) dealing with the question of the exhaustion of the supply of sodium nitrate, the author maintains that, by suitable irrigation of the soil, sufficient nitrate can be obtained for the largest wheat crops, and that the demand for nitrogenous manures could in this way be greatly diminished.

N. H. J. M.

**Utilisation by Plants of the Phosphoric Acid Dissolved by the Water of the Soil.** By TH. SCHLÖESING, jun. (*Compt. rend.*, 1898, 127, 820—822).—Maize was grown in pots containing 46 kilos. of sand and watered with Vanne water to which potassium nitrate and magnesium sulphate were added. The water contains, without further addition, sufficient lime and also 0·07 per million of phosphoric acid. Pot 1 received for some weeks this solution alone, afterwards the same solution with an additional 1 per million of phosphoric acid. Pot 2 was watered the whole time with the solution, with the addition of 2 per million (making 2·07 per million) of phosphoric acid, whilst pot 3 received no further quantity of phosphoric acid. The phosphoric acid was determined in the drainage from time to time, and, at the end of the experiment, in the produce. For some time, when the growth was still limited, the drainage water of pots 1 and 3 contained more phosphoric acid than the water applied, although the sand was very poor in phosphoric acid (23·5 per million); in the case of pot 2, the solution gave up a portion of its phosphoric acid to the soil. As the vegetation increased, the phosphoric acid of the drainage diminished considerably, especially in pot 2, in which the plants absorbed almost the whole of the phosphoric acid supplied. The yield of produce (dried at 40°) was, pot 1, 152; pot 2, 621, and pot 3, 53 grams (2 plants each pot). With wheat watered with solutions containing 0·5 and 1·0 per million of phosphoric acid, yields were obtained corresponding with 10 and 18 hectolitres per hectare.

N. H. J. M.

**Effect, on Vegetation, of Perchlorate present in Potassium Nitrate.** By AIMÉ FAGNOUL (*Ann. Agron.*, 1898, 24, 607—608; from *J. Agric. Prat.*, 1898, ii, 159).—Two per cent. of potassium perchlorate in potassium nitrate had comparatively little effect on

the growth of fescue, but larger amounts almost killed the plants. The quantity which is normally present in the ordinary nitrates used as manures, is therefore unimportant.

N. H. J. M.

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## Analytical Chemistry.

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**Colorimetric Estimation of Oxygen dissolved in Water.** By WILLIAM McD. MACKEY and R. E. MIDDLETON (*J. Soc. Chem. Ind.*, 1898, 17, 1127—1128).—Two U-tubes, each of 265 c.c. capacity, are employed. One is graduated, the other plain. Each limb is surmounted by a stopcock and funnel head, and near the bend there is a side tube with a stopcock. The ungraduated tube is filled with the water to be examined. About 5 c.c. of coal gas is introduced by the side tube, and then 5 c.c. of a 15 per cent. solution of potash is added through one funnel, and 5 c.c. of a 5 per cent. solution of pyrogallol through the other, the displaced water being drawn off at the side tube. The bubble of gas is used to mix the contents of the two limbs, and in 10—20 minutes the maximum depth of the brown coloration, due to oxygen present, is attained. Another portion of the same water is diluted with distilled water, boiled down to its original bulk to free it from oxygen, and cooled in coal gas in a flask fitted with two tubes like a wash bottle. By passing coal gas through these tubes and inverting the flask, the water is transferred to the graduated U-tube, through the side stopcock. Pyrogallol and potash are added as before, and then air is drawn in until, after agitation, the depth of colour is the same as in the other apparatus. The residual nitrogen is then transferred to one of the limbs, and its volume read off after lowering the water in the other limb to the same level. The brown coloration is fairly permanent in the absence of light, so that the reagents may be added to the water as soon as it has been collected and the comparison made in the laboratory later. As the volume of the water is in each case approximately 250 c.c. (265—15), the volume of the nitrogen gives at once cubic centimetres of oxygen per litre. M. J. S.

**Separation and Estimation of the Halogens in their Silver Compounds.** By HENRI BAUBIGNY (*Compt. rend.*, 1898, 127, 1219—1221).—Neutral solutions of potassium permanganate have no action on the halogen compounds of silver. In presence of nitric acid (sp. gr. = 1.34), however, the iodide is converted into iodate, which dissolves without loss of iodine, the bromide is decomposed, yielding free bromine and bromic acid in the cold, but at 80° the whole of the bromine is liberated; the chloride is only affected when heat is applied, chlorine being then set free. The permanganic acid, however, is destroyed under these conditions before the above reactions are completed.

When the permanganate is replaced by chromate, the iodide is

readily converted into iodate, but the chloride and bromide are only slowly attacked even at 100°. If, in addition, sulphuric acid (64—65° B.) instead of nitric acid be used, the iodide is quantitatively converted into iodate, and the bromine and chlorine are set free at a temperature of 90—95°. The following method of separating the halogen is based on this fact.

The halogens are precipitated as silver compounds, which are separated by filtration through glass wool contained in a very thin tube, which is drawn out to a fine point at one end; the tube is transferred to a flask and broken by agitation, the cold chromic acid mixture is then added and the whole heated at 90—95°, the chlorine and bromine liberated being collected by aspiration through bulbs containing alkali; the iodate formed is reduced by means of sulphurous anhydride passed into the diluted and filtered liquid, when silver iodide is precipitated in quantitative amount. If the silver iodide has a grey tint, due to the presence of reduced silver, it is only necessary to boil it for a short time with nitric acid in order to eliminate this source of error.

In some cases, when water is added to the cold chromic acid mixture, precipitation of silver chromate occurs, hence it is advisable to avoid the use of any large excess of dichromate. In case any such precipitate is formed, it should be dissolved in ammonia and reduced by means of sulphurous anhydride, any silver iodide produced being added to that obtained in the ordinary course of the experiment.

A. L.

**Estimation of Perchlorate in Chili Salpetre.** By C. AHRENS and P. HERT (*Chem. Centr.*, 1898, ii, 558; from *Zeit. öffentl. Chem.*, 4, 445—448).—Twenty grams of the powdered sample is introduced into a flat 200 c.c. platinum dish, moistened with 2—3 c.c. of cold saturated aqueous soda, 1 gram of pure manganese dioxide added, and the whole evaporated to dryness; the dish is then covered and heated to redness over a Maste burner. When cold, the fused mass is treated with 100 c.c. of hot water, allowed to cool, and then made up to 250 c.c.; 50 c.c. of the filtrate is acidified with 10—15 c.c. of nitric acid of sp. gr. = 1.20, and a 1 per cent. solution of potassium permanganate is added drop by drop until the colour is permanent for a minute, showing that all the nitrous acid has been oxidised. The chlorine is then estimated by Volhard's process, and the difference between the amounts of chlorine found before and after fusion is calculated into perchlorate. Iodides present in the sample do not interfere, as they are oxidised to iodates by the permanganate.

L. DE K.

**Estimation of Iodine in Bismuthic Iodides.** By O. SPINDLER (*Chem. Centr.*, 1898, ii, 941; from *Schweiz. Wochschr. Pharm.*, 36, 421—423).—A weighed portion of the air-dried substance is put into a small separating funnel, a little water is added, and then sufficient ferric chloride to effect solution; the liberated iodine is dissolved by adding 3—5 c.c. of chloroform, and the extraction repeated until the chloroform remains colourless. The united liquids are collected in a glass-stoppered bottle containing some water; more water is added without shaking and then poured off, to wash the chloroform, this



operation being repeated until the water runs off clear and is free from iron or bismuth oxychloride. Twenty c.c. of water and some potassium iodide are then added, and the iodine titrated, as usual, with *N*/10 sodium thiosulphate. The author states that the compounds  $\text{BiI}_3$  and  $\text{BiOI}$  can only be obtained pure by working under specified conditions; as a rule, mixtures of these salts are obtained.

L. DE K.

**Estimation of Hydrogen Sulphide, Sulphurous Acid, and Thiosulphuric Acid.** By WALTHER FIELD (*Chem. Centr.*, 1898, ii, 868—870; from *Chem. Ind.*, 21, 372—380).—*a. Estimation of Sulphides.*—The apparatus consists of an Erlenmeyer flask of 300—350 c.c. capacity, the doubly perforated rubber cork of which is fitted with a stopcock funnel tube reaching to the bottom of the flask, and connected at the top with the delivery tube of a carbonic anhydride apparatus. There is also a delivery tube connected with a series of four Geissler's potash bulbs and an aspirator. Of these, the first set of bulbs is empty, the second and third are filled with *N*/10 solution of iodine, and the fourth contains *N*/10 sodium thiosulphate. The aspirator regulates the current of carbonic anhydride. After the apparatus has been freed from air by a current of carbonic anhydride, the solution containing the sulphide is introduced into the flask, 20 c.c. of a 25 per cent. solution of magnesium chloride is added, and the liquid is boiled, the gas being passed meanwhile. All the sulphur is now expelled as hydrogen sulphide, which is absorbed in the bulbs and titrated in the usual way.

*b. Estimation of Sulphurous Anhydride.*—The same apparatus is used, the decomposition being effected with dilute hydrochloric acid.

*c. Estimation of Thiosulphates.*—The salt is first converted into the tetrathionate by means of iodine, and the solution is then reduced in the apparatus by means of hydrochloric acid and sheet aluminium. All the sulphur is thus given off as hydrogen sulphide.

*d. Estimation of Thiosulphates in the Presence of Sulphites.*—The mixture is first oxidised with iodine, and the thiosulphate is then found by estimating the amount of hydrogen sulphide given off by the acid aluminium treatment.

*e. Estimation of Sulphites in the Presence of Thiosulphates.*—The mixture is treated with mercuric chloride and then with hydrochloric acid; the sulphurous anhydride evolved is absorbed by the iodine and found by titration. A precipitate consisting of mercuric sulphide, due to the thiosulphate, remains in the flask unaffected by the acid.

*f. Estimation of Sulphides, Sulphites, and Thiosulphates in the Presence of each other.*—The sulphide is estimated by the process *a*; mercuric chloride is then added as in *e*, and the residue in the flask, after being oxidised with iodine, is treated with aluminium as in *c*.

*g. Estimation of Sulphides of Alkalis or Earthy Metals, Polysulphides, Sulphites, and Thiosulphates in the Presence of Free Sulphur and Metallic Sulphides.*—1. *Free Sulphur.* This is easily extracted by means of carbon bisulphide. 2. *Sulphides.* Their hydrogen sulphide is readily estimated according to the directions given in *a*. 3. *Polysulphides.* The liberated sulphur may be recovered by agitating the liquid in the

flask with carbon bisulphide; a fraction of the sulphur may have combined with the sulphite to form thiosulphate. 4. *Ferrous Sulphide*. The residue from 3 is oxidised with iodine, and the liberated sulphur again extracted with carbon bisulphide. 5. *Thiosulphate*. The residue from 4, or another portion of the original liquid, is oxidised with iodine and then treated according to *c*; in the presence of polysulphides, the result will be too high. 6. *Sulphites*. These cannot be present in a solution of polysulphides, but the mixture may occur in a solid mass; this is then placed in a solution of mercuric chloride, and the unaffected sulphite decomposed as directed in *e*. L. DE K.

**Volumetric Estimation of Combined Sulphuric Acid.** By FÉLIX MARBOUTIN and MARCEL MOLINIÉ (*Bull. Soc. Chim.*, 1897, [iii], 17, 950—952).—The method employed by Windish for the estimation of sulphuric acid requires the use of exactly equivalent solutions of barium chloride and potassium chromate. The authors give an account of a method by which the required correction may be accurately determined when this condition is not fulfilled. A. L.

**Volumetric Method for the Estimation of Combined Sulphuric Acid.** By FÉLIX MARBOUTIN (*Bull. Soc. Chim.*, 1897, [iii], 17, 953—955).—The sulphuric acid is precipitated by means of excess of barium chloride in acid solution, the remaining barium being then precipitated by excess of chromate in neutral or faintly alkaline solution; the residual chromate is then determined by means of arsenious acid and iodine in the usual manner. A blank experiment is made in which the same volumes of barium chromate and arsenic solutions are used, when the difference in volume of the iodine solution required in the two experiments represents the amount of sulphuric acid present in the first experiment. The advantage of the method lies in the fact that no washings or filtrations are necessary, and the iodine solution is the only one which need be accurately standardised. A. L.

**Estimation of Sulphuric Acid in the Presence of Iron.** By FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1898, 19, 97—103).—When a solution of sulphuric acid containing ferric chloride is precipitated with barium chloride, the precipitate contains ferric sulphate, and the results obtained are too low, and vary according to the amount of ferric chloride which is present. Accurate results can, however, be obtained either by precipitating the iron with ammonia, or by converting the iron into a complex salt, which does not come down with the barium sulphate.

The solution of sulphuric acid and ferric chloride is precipitated in the cold with a slight excess of ammonia, the mixture heated to near the boiling point, and precipitated with barium chloride, an excess of dilute hydrochloric acid added, and, after remaining for some time in order to completely dissolve the ferric hydroxide, the clear liquor is decanted through a filter. The precipitate is washed with cold hydrochloric acid a few times, and then treated in the ordinary way. The results are accurate to about 0.07 per cent.

The second method consists in adding to the sulphuric acid solution

either ammonium oxalate or ammonium tartrate, and ammonia, and precipitating with barium chloride; the precipitate being then treated with hydrochloric acid as described above, accurate results are obtained.

E. C. R.

**Iodometric Experiments.** By GUNNER JÖRGENSEN (*Zeit. anorg. Chem.*, 1898, 19, 18—36).—Riegler's statement that sodium thiosulphate can be titrated with iodic acid has been disputed by Walker (*Abstr.*, 1898, ii, 139). The present paper deals with some of the causes of error in this reaction. Potassium iodate, in the presence of ammonium chloride, oxidises sodium thiosulphate to tetrathionate, a small quantity of sulphate being also formed, and the solution becoming alkaline; no ammonia is, however, destroyed. Potassium iodate in the presence of ammonium chloride oxidises sodium tetrathionate to sulphate, and this reaction also takes place when potassium iodide is present. In solutions containing ammonia, potassium iodate converts sodium tetrathionate into sulphate, and probably small quantities of other oxidation products of sulphur are formed, and a very small quantity of ammonia is destroyed. Iodine in ammoniacal solutions reacts with tetrathionate in a similar manner to potassium iodate; also it converts sodium thiosulphate into a mixture of sulphate and tetrathionate with some loss of ammonia. In neutral solutions, sodium tetrathionate is oxidised by iodine to sulphate, and the solution becomes strongly acid. Sodium thiosulphate is converted into a mixture of tetrathionate and sulphate by a solution of potassium iodate containing hydrochloric acid.

From the above, it is evident that ammonia cannot be titrated by Kjeldahl's iodometric method, namely by being left in contact with excess of thiosulphate, and then estimating the excess of the latter with iodine.

E. C. R.

**Testing Milk for Nitrates.** By EDWIN ACKERMANN (*Chem. Centr.*, 1898, ii, 504—505; from *Schweiz. Wochschr. Pharm.*, 36, 285—287).—Ten c.c. of the milk is mixed with 2 drops of a 20 per cent. solution of calcium chloride, and heated, first at 50° and then for 10 minutes at 100°. The whey is then tested as follows: 0.5 c.c. is dropped slowly on to 2 c.c. of a solution of diphenylamine contained in a watch-glass, taking care not to mix the solutions. If nitrates are present, a blue ring will form after a few minutes; if not, there will be a brownish spot; the test is extremely delicate. The reagent is made by dissolving 0.02 gram of diphenylamine in 20 c.c. of dilute sulphuric acid (1 : 3), and then making up to 100 c.c. with strong sulphuric acid.

L. DE K.

**Reduction of Nitric Oxide by Copper, with Special Reference to Dumas' Method of Estimating Nitrogen.** By THOMAS GRAY (*J. Soc. Chem. Ind.*, 1898, 17, 741—743; 829).—Although many chemists have experienced a difficulty in reducing the nitric oxide evolved in a combustion of a nitrogenous substance by means of a heated roll of copper gauze, the author finds that a spiral 5 inches long, tightly rolled and strongly heated, will complete the reduction even when the gas is passed at a much quicker rate than is usual in such combustions. A spiral which has been used repeatedly is more

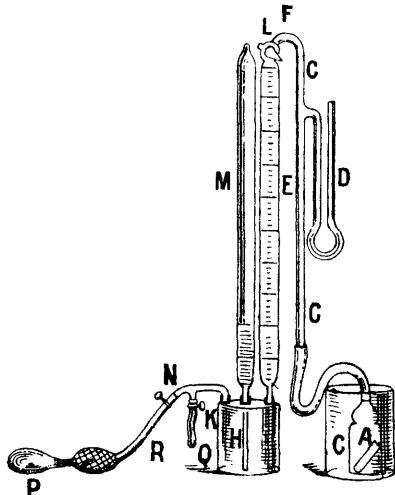
efficient than a fresh one. A very high temperature is the greatest safeguard against incomplete reduction, and the current of carbonic anhydride employed to expel the air from the tube should be stopped whilst the combustion is taking place.

M. J. S.

**Estimation of Carbonic Anhydride in Minerals.** By ARTHUR MARSHALL (*J. Soc. Chem. Ind.*, 1898, 17, 1106—1107).—The apparatus consists of a gas generating vessel, A, a gas measuring tube, E, and a gas reduction tube, M, acting on the same principle as that in Lunge's gas volumeter, E and M dip into refined petroleum oil of high boiling point, contained in H, in which carbonic anhydride is very sparingly soluble. D is a mercury manometer, P, Q, R, N, appliances by which the pressure in H can be adjusted. The three-way stopcock L (which is imperfectly described), allows E and G to be connected, or either of them separately to be placed in communication with the external atmosphere.

Having forced the petroleum to the top of E, placed the weighed substance in A, and 1 c.c. of concentrated hydrochloric acid in the small glass tube B, A is brought to atmospheric temperature by immersing it in the water contained in C, and to atmospheric pressure by means of L; E and G are then connected, the carbonate is decomposed, keeping A in the water, by which means volatilisation of hydrochloric acid is prevented, the pressure is brought to equality with the atmosphere, and then, after closing L, it is again adjusted until the gas in M occupies the standard volume. The reading of E then gives at once the volume of carbonic anhydride at 0° and 760 mm. By using concentrated acid, the error due to carbonic anhydride remaining in solution is reduced to a minimum, and there is a small compensating error when the level of the petroleum in E is higher than that in M.

M. J. S.



**Action of an Alkaline Solution of Formaldehyde on Silver Haloids and Thiocyanate.** By LUDWIG VANINO (*Ber.*, 1898, 31, 3136—3139).—These silver salts can be reduced quantitatively to metallic silver by pouring caustic potash or soda over them in a porcelain dish and adding formaldehyde solution; as a rule, the reaction is complete in a few minutes. In the case of silver bromide, it is necessary to warm if the solution is dilute; in the case of silver iodide, it is necessary to boil, and to add formaldehyde repeatedly. For reducing silver chloride, aqueous potassium or sodium carbonate may

be used instead of the hydroxide, the solution being warmed gently ; fused silver chloride, however, is only reduced under these circumstances when powdered, and the solution should be boiled.

This method may be adopted conveniently for recovering silver from the residues obtained in the titration of that metal with thiocyanate solution ; a residue of pure silver is obtained, any iron compound mixed with the original solid going into solution ; the residue is simply washed with water.

C. F. B.

**Electrolytic Estimation of Zinc.** By HEINRICH PAWECK (*Chem. Centr.*, 1898, ii, 872—873 ; from *Österr. Zeit. Berg-Hütt.*, 46, 570—573).—In order to facilitate the electric separation of zinc, Vortmann has proposed to add to the solution a known weight of mercuric chloride ; the zinc then separates as amalgam, and allowance is made for the amount of mercury deposited.

The author has noticed that in this process the platinum cathodes are attacked and lose in weight ; the addition of mercuric chloride is also inconvenient. He now proposes using amalgamated brass wire gauze cathodes, so as to prevent hydrogen bubbles from adhering to the cathode and, consequently, the formation of spongy zinc. Two circular pieces of the gauze of 6 cm. diameter are well cleaned and covered by means of electrolysis with the mercury obtainable from 0.6 gram of mercuric chloride, washed with alcohol and ether, and dried at 30—40°. The zinc solution must contain potassium sodium tartrate and alkali ; the tension should be from 2.65—3.60 volts, and the current 0.1—0.5 ampère. After gently washing and drying at 30—40°, the wire gauze is reweighed. The test analyses are satisfactory.

By using a brass wire gauze electrode, the zinc may be also deposited in a crystalline condition without amalgamation. The liquid, which must contain free acid but be free from iron, is electrolysed at 50—60°, using tensions of 3.4—3.55 volts and a current of 0.3—0.7 ampère.

L. DE K.

**Estimation of Lead in Lead Ores.** By LEOPOLD SCHNEIDER (*Chem. Centr.*, 1898, ii, 559—560 ; from *Österr. Zeit. Berg-Hütt.*, 46, 431—434).—The author recommends the following process : 1 gram of the ore (galena) is boiled in a covered 200 c.c. beaker with 5 c.c. of strong hydrochloric acid for 10—15 minutes, and 5 c.c. of strong nitric acid is then added ; as soon as red fumes cease to be evolved, 10 grams of tartaric acid dissolved in 25 c.c. of water is added and the heating is continued for a short time. When cold, 25 c.c. of strong ammonia is added, and the liquid heated and filtered from any undissolved siliceous matter or barium sulphate, the filter being well washed with a weak alkaline solution of ammonium tartrate ; the filtrate is then diluted to about 300 c.c., 50 c.c. of dilute sulphuric acid (1:1) is added to precipitate the metal as sulphate, and this is washed with water containing 1 per cent. of sulphuric acid, dried, ignited, and weighed. To the weight obtained, 0.003 gram should be added to compensate for the slight solubility of lead sulphate.

L. DE K.

**Detection of Manganese.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1898, ii, 942; from *Boll. Chim. Farm.*, 37, 545—546).—Instead of testing for manganese by the formation of permanganic acid on heating the substance with nitric acid and lead dioxide, the author prefers acting in the cold with dilute sulphuric acid and a few crystals of potassium bromate. A gradually increasing reddish-violet colour due to permanganic acid is developed. The reaction is not given by chlorates or iodates.

L. DE K.

**Valuation of Iron and Manganese Ores.** By PAUL LEHNKERING (*Chem. Centr.*, 1898, ii, 507—508; from *Zeit. öffentl. Chem.*, 4, 459—464).—*Estimation of Iron in Ores.*—The quick processes usually employed are not trustworthy if the ores contain organic matter, or insoluble ferruginous silicates, or sulphides; the presence of titanium, arsenic, or copper compounds also interferes.

The following process is recommended by the author in the case of reference analyses. Five grams of the finely powdered and dried ore after being ignited in a porcelain crucible for half an hour over a Bunsen flame to destroy any organic matter, is heated in an Erlenmeyer flask with 60 c.c. of hydrochloric acid of sp. gr. = 1.19 on the water-bath for 4 hours, evaporated to dryness, the residue dissolved in hydrochloric acid, 100 c.c. of hot water added, and the insoluble matter washed with hot dilute hydrochloric acid. The residue is then dried and fused in a platinum crucible with 5 grams of sodium potassium carbonate and a little nitre, and when cold, the fused mass is dissolved in hydrochloric acid and the solution evaporated with the addition of sulphuric acid. The residue, dissolved in dilute hydrochloric acid, is filtered, and the iron in the filtrate precipitated by ammonia, washed, redissolved in dilute hydrochloric acid and the solution added to the main liquid. Any arsenic or copper is now precipitated by hydrogen sulphide, the excess of the latter being removed by boiling and treating with potassium chlorate; after boiling off the chlorine, the iron is titrated, preferably by the stannous chloride-permanganate method.

*Estimation of Manganese in Ores.*—The author does not recommend the volumetric processes, but prefers estimating the metal as sulphide. The ore is first dried at 120°, and any matter insoluble in hydrochloric acid must always be fused with sodium potassium carbonate to recover any insoluble manganese.

Silica obtained from iron or manganese ores may be contaminated with insoluble sulphates or titanous acid; the latter may be separated by fusing with potassium hydrogen sulphate and extracting the fused mass with cold water. The mixture of silica and insoluble sulphates is then weighed and heated with sulphuric and hydrofluoric acids; the loss represents silica.

L. DE K.

**Sources of Error in the Electrolytic Estimation of Iron.** By SAMUEL AVERY and BENTON DALES (*Ber.*, 1899, 32, 65—68).—The authors have made careful estimations of iron by the usual electrolytic methods, and have found that, in all cases, a certain amount of carbon is deposited together with the iron. When the estimation is carried out in ammonium oxalate solution (Classen), some 0.22 per cent. of the deposit consists of carbon, and a small quantity of iron still remains

in solution. In citric acid solution, as much as 2 per cent. of the deposit often consists of carbon, compare Smith (*Elektro. Analyse*, 92), Nicholson and Avery (Abstr., 1896, ii, 627), Heidenreich (*ibid.*, ii, 545). When Moore's method (Abstr., 1886, 921) of depositing the iron from ammonium metaphosphate solution is employed, some 2 per cent. of carbon and phosphorus is also deposited. J. J. S.

**Colorimetric Estimation of Iron.** By E. EWERS (*Chem. Centr.*, 1898, ii, 605—606; from *Apoth. Zeit.*, 13, 536—538).—The author rejects the use of potassium ferrocyanide for the colorimetric estimation of iron, but recommends using potassium thiocyanate. To oxidise traces of iron often found in waters or in the ash of wine, it is best to use a mixture of sulphuric and nitric acids instead of hydrochloric acid and potassium chlorate, as hydrochloric acid is seldom quite free from iron. Gerhard's tannin method is also strongly recommended. One hundred c.c. of the sample of water is mixed with 20 c.c. of a solution of sodium pyrophosphate (1:20) and 5 drops of tannin solution (1:20 dil. alcohol). The colour is then compared with that produced by means of a standard solution of iron (0.895 gram potassium iron alum and 2.5 grams of sodium pyrophosphate in a litre of water). If part of the iron has become oxidised and insoluble, it may be dissolved by means of a little oxalic acid and a little potassium citrate; the excess of oxalic acid must then be removed by calcium carbonate.

To estimate iron in milk, 200 c.c. of the sample is incinerated, and the ash fused with its own weight of sodium carbonate and a little potassium carbonate and nitrate; the phosphates are decomposed and rendered soluble and may be removed by hot water. The insoluble matter containing the iron is then dissolved in 10 c.c. of dilute hydrochloric acid and tested in a colorimeter with potassium thiocyanate.

L. DE K.

**Volumetric Estimation of Bismuth.** By O. SPINDLER (*Chem. Centr.*, 1898, ii, 584; 607—608; from *Schweiz. Wochschr. Pharm.*, 36, 326—328; 333—335).—The nitric acid solution of the bismuth or an emulsion of basic bismuth nitrate is heated with excess of normal potash until the hydroxide has separated, and the excess of alkali is then titrated with normal hydrochloric acid, using phenolphthalein as indicator; the amount of nitric acid is thus found. A measured excess of accurately titrated 25 per cent. hydrochloric acid is now added to dissolve the precipitate, and the excess of acid is removed by means of normal potash; this causes the bismuth to separate as oxychloride. After decolorising the liquid with a drop of dilute acetic acid, the chlorine remaining in the liquid is estimated by means of standard silver nitrate. The difference between chlorine added and chlorine found represents an equivalent quantity of bismuth oxychloride. To apply the process to organic preparations of bismuth, these must be mixed with four times their weight of dry sodium carbonate, and gradually introduced into an iron crucible containing fusing nitre; the mass is first extracted with water, and the insoluble matter is dissolved in nitric acid and treated as directed.

L. DE K.

**Volumetric Estimation of Gold and Platinum.** By HEINRICH PETERSON (*Zeit. anorg. Chem.*, 1898, 19, 59—66).—The method consists in treating the solution of the metallic salt with excess of potassium iodide, and then estimating the liberated iodine with a solution of sodium thiosulphate.

The solution of the platinum in the form of potassium platonic chloride is added to the potassium iodide solution, and the dark brown mixture titrated with sodium thiosulphate until a pure lemon-yellow coloration is obtained. The results are accurate, and very small quantities of platinum can be estimated by this method. The reaction takes place according to the equation  $\text{PtCl}_4 + 4\text{KI} = \text{PtI}_2 + \text{I}_2 + 4\text{KCl}$ .

The solution of the gold either as auric chloride or sodium auric chloride is treated in a similar manner, but starch solution is used as an indicator, and the dark green mixture is titrated with sodium thiosulphate until a rose coloration is obtained. The reaction takes place according to the equations:  $\text{AuCl}_3 + 3\text{KI} = \text{AuI} + 2\text{I} + 3\text{KCl}$  and  $\text{AuI} + \text{Na}_2\text{S}_2\text{O}_3 = \text{NaI} + \text{NaAuS}_2\text{O}_3$ , therefore 3 molecules of sodium thiosulphate are required for 1 molecule of auric chloride.

E. C. R.

**Estimation of Small Quantities of Methylic Alcohol, Formaldehyde, and Formic Acid.** By MAURICE NICLOUX (*Bull. Soc. Chim.*, 1897, [iii], 17, 839—840).—The author has applied his volumetric process for the estimation of alcohol (*Abstr.*, 1898, ii, 543), based on the oxidation of the latter by a solution of potassium dichromate in sulphuric acid solution, to the estimation of small quantities of methylic alcohol, formaldehyde, and formic acid. With solutions containing up to 0.1 per cent. of these substances, and in the absence of other reducing organic compounds, the results obtained are more accurate than those given by any other process.

N. L.

**Indirect Estimation of Extractive Matter [in Alcoholic Beverages].** By WILHELM FRESenius (*Zeit. anal. Chem.*, 1899, 38, 35—37).—In estimating the percentage of extractive matter by the Windisch or Halenke and Möslinger tables, the safer course is to calculate the gravity of the dealcoholised liquid from the original gravity and the percentage of alcohol found, instead of ascertaining the actual gravity after distilling off the alcohol, for in any case where saccharose and an organic acid are simultaneously present the inversion of the saccharose which takes place during the distillation would lead to a higher and less correct result being obtained by the latter course.

M. J. S.

**Detection of Glycerol.** By LEO GRÜNHUT (*Zeit. anal. Chem.*, 1899, 38, 37—42).—On applying to some samples of chicory-coffee the methods employed for the estimation of glycerol in wine (Borgmann and W. Fresenius, *Anleitung zur Chemischen Analyse des Weines*, 2nd ed., p. 50), considerable amounts of residue were obtained, which, however, did not seem to be glycerol. An attempt to examine these "crude glycerol" residues by the permanganate oxidation method furnished in all cases small quantities of oxalic acid, but left the



question open whether these were in reality derived from glycerol. The desired end was at last attained by distilling the residues with potassium hydrogen sulphate and examining the distillates for acraldehyde by treatment with a mixture of ammoniacal silver nitrate and sodium hydroxide. In none of the cases could acraldehyde be detected, although the method was proved to be a trustworthy one. There appears, therefore, to exist in chicory-coffee some substance which agrees with glycerol both as to its solubility in alcohol and ether-alcohol, and in yielding oxalic acid when oxidised by alkaline permanganate, and which, nevertheless, is not glycerol. M. J. S.

**Kjeldahl's Process for Estimating Sugar.** By GUSTAV BRUHNS (*Chem. Centr.*, 1898, ii, 903—905; from *N. Zeit. Rüb.-Zucker-Ind.*, 41, 105—112, also *Zeit. anal. Chem.*, 38, 73—96).—The paper is devoted to a criticism of Kjeldahl's sugar process (*Abstr.*, 1896, ii, 580).

The conclusions arrived at are as follows. 1. There is no need for operating in a current of hydrogen. 2. It is better to boil the sugar solution with the Fehling's solution for a few minutes, than to heat for 20 minutes in a water-bath. 3. It is preferable to use the Soxhlet's modification of the Fehling's solution, as it contains less alkali. 4. It is best to mix the solution of the copper sulphate with the alkaline solution of potassium sodium tartrate just before use. The cuprous oxide is best collected on a Schleicher filter instead of an asbestos filter; the amount of soluble copper retained by the paper is very trifling. 5. It has been positively proved that prolonged boiling with even pure cane sugar precipitates a large quantity of cuprous oxide, so that the Kjeldahl process gives results which are too high should cane sugar be present. L. DE K.

**Colorimetric Estimation of 'Invert' Sugar.** By D. SIDERSKY (*Chem. Centr.*, 1898, ii, 648; from *Bull. Assoc. Chim.*, 15, 1134).—The process is based on the fact that Fehling's solution is reduced, and consequently more or less decolorised, by invert sugar at the boiling temperature; the solution may then be compared in a colorimeter with the same mixture of copper solution and cane sugar which has not been boiled. From the loss of colour, the amount of copper reduced, and consequently the invert sugar, is readily calculated. L. DE K.

**Detection of Cane Sugar in Milk.** By CAYAUX (*Chem. Centr.*, 1898, ii, 510; from *Pharm. Centr.-Halle.*, 39, 503—504).—The author recommends the resorcinol test; 10 c.c. of the sample is boiled with 0.1 gram of resorcinol and 1 c.c. of hydrochloric acid for 5 minutes; if cane sugar is present, the liquid becomes rose red. Adulteration of milk with coco-nut juice which contains natural cane sugar may also be detected by means of the resorcinol test. L. DE K.

**The Most Important Sweetening Materials.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1899, 38, 20—30).—The author has drawn up a scheme for the employment of a small number of characteristic reagents in discriminating saccharose, dextrose, levulose, lactose, galactose, maltose, ammonium-glycyrrhizin, glycerol, and "saccharin." The reagents proposed are (a) Fehling's solution; (b) a cold saturated

solution of ammonium molybdate; (c) Böttger's reagent, basic bis-muth nitrate and soda solution; (d) a solution of  $\alpha$ -naphthol in dilute

Reagent.	<i>a.</i>	<i>b.</i>	<i>c.</i>		<i>d.</i>	<i>e.</i>	
			Sedi- ment.	Upper liquid.		Upper layer.	Lower layer.
Saccharose ...	No reduction	Feebly bluish after some time	No change		Intense violet- blue	Pale yellow	Rasp- berry red
Dextrose .....	Reduction in the cold	As saccharose	Black	Yellow	No reaction	Pale yellow	Colour- less
Levulose .....	As dextrose	Cornflower blue	As dextrose		Amber- yellow	Pale yellow	Rasp- berry red
Lactose .....	Reduction on warming	As saccharose	Feebly yellow	In- tensely yellow	Deep amber- yellow	As dextrose	
Galactose.....	Reduction, slowly in the cold, rapidly on heating	A some- what deeper blue than saccharose	Grey	Colour- less	No colour	Colour- less	Lemon yellow
Maltose ...	As dextrose	No colour	Feebly brown	In- tensely yellow	Deep violet	As dextrose	
Glycyrrhizin .	Reduction on boiling	No colour			No characteristic result		
Glycerol .....	No reduction	No reaction			Greenish after 1—2 hours		
Saccharin .....	No reduction	No reaction			No colour	Pale yellow	Milky white, then a greenish irides- cent deposit

alcohol; (e) sesamé oil. Tests *b* and *c* are performed by mixing the reagent with an equal volume of a 5 per cent. solution of the substance, heating in a water-bath to  $100^{\circ}$ , and allowing to cool; *d* is applied by putting 1 c.c. of a 1 per cent. solution of the substance in a test-tube, pouring down the side 0.3 c.c. of concentrated sulphuric acid, and covering with about 1 c.c. of the naphthol solution; the colour appears in the contact zone. Test *e* is the converse of Baudouin's reaction for sesamé oil; equal volumes of the oil and hydrochloric acid, with half the volume of the saccharine substance, are vigorously shaken, then left in repose, and the colours of the two layers observed.

Besides the above reactions, the most salient physical properties of the substances, such as solubility, fermentability, optical activity, &c., are briefly described. M. J. S.

**Estimation of Glycogen in Meat Extracts.** By GEORG LEBBIN (*Chem. Centr.*, 1898, ii, 513; from *Pharm. Zeit.*, 43, 519).—Twenty-five grams of extract of meat is dissolved in water, and the solution, made up to 100 c.c., is mixed with 100–150 c.c. of 90 per cent. alcohol containing 4 per cent. of potassium hydroxide; after 1–2 hours, the liquid is filtered, and the residue, after being washed with the alkaline alcohol, is dissolved in 50 c.c. of water slightly acidified with dilute hydrochloric acid, and precipitated with 10 c.c. of mercuric potassium iodide, made by dissolving 20 grams of mercuric chloride in 300 c.c. of water, adding 20 grams of potassium iodide dissolved in 100 c.c. of water, and then more mercuric chloride solution until the precipitate no longer redissolves. After half an hour, the liquid is filtered and the precipitate washed with hot water; on adding an equal bulk of 95 per cent. alcohol to the filtrate, the glycogen is precipitated, and, after being washed with alcohol and ether, is dried and weighed. L. DE K.

**Detection and Estimation of Citral.** By FERDINAND TIEMANN (*Ber.*, 1898, 31, 3324–3340).—See this vol., i, 249.

**Detection and Estimation of Acetone by Means of Mercuric Sulphate.** By GEORGES DENIGÈS (*Compt. rend.*, 1898, 127, 963–965).—If the product of the action of acetone on mercuric sulphate (this vol., i, 22) is dried in a vacuum or at a temperature not exceeding  $100^{\circ}$ , its composition is  $(2\text{HgSO}_4, 3\text{HgO})_3, 4\text{COR}_2$ , and not  $2\text{HgSO}_4, 3\text{HgO}, \text{COR}_2$ . The formation of this compound can be utilised for the detection and estimation of small quantities of acetone in water, methylic and ethylic alcohols, &c., provided that the aqueous solution does not contain more than 1 per cent., and the methylic alcohol does not contain more than 2 per cent. The reagent, prepared by dissolving 5 grams of mercuric oxide in 100 c.c. of water and 20 c.c. of sulphuric acid, must be used in large excess.

Two c.c. of the liquid and 2 c.c. of the reagent are mixed in a test-tube, and heated at  $100^{\circ}$  in a water-bath for 10 minutes; if at the end of that time there is no turbidity, no acetone is present. Even with 0.1 gram of acetone in 2 c.c., the precipitate does not form before 45 seconds. In the case of methylic alcohol, 2 c.c. are mixed with

2 c.c. of water and 4 c.c. of reagent; ethylic alcohol must be diluted until the alcoholic strength of the liquid does not exceed  $2^{\circ}$ .

For quantitative estimation, 25 c.c. of the liquid and 25 c.c. of the reagent are heated at  $100^{\circ}$  for 10 minutes in a strong closed flask of about 90 c.c. capacity, and the precipitate is collected, dried, and weighed. Another method is to dilute the liquid to 100 c.c., withdraw 20 c.c., add 15 c.c. of dilute ammonia solution (1:5), 10 c.c. of decinormal potassium cyanide solution, and then titrate with decinormal silver nitrate, using potassium iodide as indicator. If  $n$  = the volume of silver solution, and  $x$  = the quantity of acetone per litre of the original liquid,  $x = (n - 0.4) \times 0.3$ .

The ethylic alcohol present must not exceed  $1^{\circ}$ , and the methylic alcohol must not exceed  $10^{\circ}$ .  
C. H. B.

**Detection of Tartaric Acid in Presence of Oxalic Acid.** By WILHELM FRESENIUS (*Zeit. anal. Chem.*, 1899, **38**, 33—35).—Tartaric acid cannot be separated from oxalic acid by methods based on the difference in the solubilities of the calcium salts in acetic acid. On adding calcium chloride to acetic acid solutions of the two organic acids, oxalic acid produces a precipitate instantly, tartaric acid only after some time, so that the presence of tartaric acid is no obstacle to the detection of oxalic acid; but in a mixed solution, the calcium oxalate carries down the calcium tartrate almost completely. The methods laid down in Fresenius' "Qualitative analysis" permit of the detection of both acids as well as of citric acid, when occurring together.

M. J. S.

**Analysis of Mixtures of Ortho-, Meta-, and Para-nitrobenzoic Acids.** By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1898, **17**, 335—345).—The method described is based on the difference in the solubilities of the three acids in water at  $25^{\circ}$  (this vol., i, 141); 50 c.c. of water saturated at this temperature with the ortho-acid alone is neutralised by 21.1 c.c. of  $N/10$  baryta; solutions of the meta- and para-acids prepared in the same manner alone neutralise 10.0 and 1.0 c.c. of the alkali. A mixture of the ortho- and meta-acids neutralises 32.2 c.c. of the baryta, whilst mixtures of the para- with the ortho- and with the meta-acid neutralise respectively 22.1 and 11.0 c.c. (compare *loc. cit.*). The method adopted in the analysis is as follows. A weighed quantity of the mixture of acids (1—1.5 grams) is shaken in a bottle during 3 hours with 50 c.c. of water until the latter is completely saturated; 25 c.c. of the solution is then titrated against decinormal baryta, using phenolphthalein as indicator, and the remainder of the solution rapidly filtered with the aid of the pump. The residue is then extracted successively with fresh quantities of water, using 50 c.c. each time, the total amount of acid dissolved by each being determined by decinormal baryta, until the residue finally remaining consists of one of the acids only, in a pure state. This is then weighed, whilst the amount previously dissolved is calculated by taking into account its solubility in the various portions which have previously had their total acidity determined; in the case of mixtures containing both the ortho- and meta-acid, allowance must be made for their increased solubility in presence of one another. A large number of results

are given indicating the accuracy of the method, and the means of applying it to mixtures containing two only or all three of the acids simultaneously.

By means of this process, the author finds that the product obtained on nitrating benzoic acid by Gerland's method (*Annalen*, 1854, 91, 186), after being freed from sulphuric acid by washing with water, and from unchanged benzoic acid by steaming, contains 6.9 per cent. of ortho-, 1.1 per cent. of para-, and 92.0 per cent. of meta-nitrobenzoic acid; the amount of the ortho-acid actually formed is, however, probably greater than here given, some being dissolved during the removal of the sulphuric acid.

W. A. D.

**The Refraction Constant in Oil and Fat Analysis.** By HENRY R. PROCTER (*J. Soc. Chem. Ind.*, 1898, 17, 1021—1025).—The value of the information obtainable from a determination of the refractive index of a fat can be considerably enhanced by calculating the specific refractive energy or refraction constant. The formula proposed by Gladstone and Dale  $(n-1)/d$ , where  $n$  = index of refraction and  $d$  = density, is fairly constant within the range of temperature suitable for such observations, but the expression  $n^2 - 1/(n^2 + 2)d$ , introduced by Lorenz and Lorentz, is still more closely constant, especially under extreme conditions, and is better adapted for calculating the refractive energy of a compound from the refraction equivalents of the elements.

The author gives a brief account of the Zeiss-Abbe refractometer, tables of the specific gravities, also refractive indices and refraction constants of a number of the commoner oils, fats, and fatty acids from his own determinations, and of the specific refractions of the chief fatty acids and glycerides calculated from the atomic refractions determined by Conrady, and indicates the manner in which a knowledge of these values may be applied to fat analysis.

M. J. S.

**Volatile and Insoluble Fatty Acids of Butter.** By ROBERT HENRIQUES (*Chem. Centr.*, 1898, ii, 797—798; from *Chem. Rev. Fett. Harz-Ind.*, 5, 169—172).—This is a preliminary investigation intended to throw more light on the subject of edible fats.

The author has attempted to estimate the amount of volatile and easily soluble fatty acids in butter. The distillate obtained when applying the Reichert-Meissl test, after being carefully titrated, was evaporated to dryness and the residue further dried until the weight was constant. From the weight of the soap, the amount and average molecular weight of the acids may be calculated by means of the Reichert-Meissl number. The percentage of potash soap is called the "soap-figure." Calling this  $a$ , and the R.-M. figure  $b$ , the percentage of the volatile easily soluble acids equals  $a - 76b/1000$ , and the average molecular weight of the same equals  $1000 a/2b - 38$ . Analyses of different butter-fats showed that whilst the molecular weights of the acids were almost the same, the amounts of acids were lower in the case of abnormal samples; the process is, therefore, at present, not adapted for the detection of butter mixtures.

The author has constructed a table showing the various analytical butter-figures, the results being obtained as follows. Five grams of fat

is saponified with 25 c.c. of normal alcoholic potash, 10 c.c. of water is added, and the excess of alkali titrated with  $N/2$  sulphuric acid; after adding a few drops of alkali, the alcohol is distilled off, 100 c.c. of water and 40 c.c. of dilute sulphuric acid (1 : 5) are added, and 110 c.c. is distilled off; 100 c.c. of this is then titrated with  $N/10$  potash. The number of c.c. used multiplied by 1.1 represents the R.-M. number. The neutralised liquid is evaporated to dryness, and the weight of the residue, multiplied by 0.022, gives the soap figure, from which the percentage of free acids and their molecular weight are found by the above formulæ. The amount of easily volatile and soluble acids in butter of normal R.-M. figure is from 5—6 per cent.; in abnormal samples, from 4—5 per cent. Their average molecular weight varies from 93.3—99.8 per cent.

L. DE K.

**Cause of Rancidity of Butter.** By CARL AMTHOR (*Zeit. anal. Chem.*, 1899, 38, 10—20).—It has hitherto not been found possible to give numerical expression to the degree of rancidity of butter, and most of the chemists who have investigated the subject have arrived at discordant views as to the nature of the changes which produce rancidity. The author brings forward experiments which show that the development of rancidity is accompanied, not only by a large increase in the total acidity, and a smaller, but still very evident, increase in the amount of volatile acids, but that there is at the same time a production of volatile ethylic salts, principally ethylic butyrate, with small amounts of the salts of higher fatty acids. In the initial stages of rancidity, the volatile acids, chiefly butyric acid, predominate, and conceal the odour of the ethylic butyrate, but as the change progresses the latter becomes the more conspicuous. A loss of both volatile acids and volatile ethereal salts occurs on keeping, so that in very old butter none of the latter can be found, and in this state the butter has only a feeble odour resembling tallow. These changes are undoubtedly brought about by micro-organisms, which produce alcohol from the lactose, and at the same time split up the glycerides, especially the butyrin, the glycerol undergoing further changes which result in the formation of aldehydes and ketones. Since even fresh butter yields saponifiable substances when distilled, it would seem that the proportion of ethylic butyrate and volatile fatty acids should be employed as the criterion of rancidity. The co-operation of butter analysts in further investigation in this direction is invited.

M. J. S.

**Analysis of Fats. VI. Detection of Cotton-seed Oil in Lard.** By A. BÖMER (*Chem. Centr.*, 1898, ii, 646—648; from *Zeit. Unters. Nahr-Genussm.*, 1898, 532—552. Compare this vol., ii, 191, 192).—The paper is chiefly devoted to a criticism of the processes proposed for the detection of cotton-seed oil in lard. Owing to the peculiar nature of American lard, neither the iodine absorption of the sample nor that of its liquid fatty acids is of much use to detect the adulteration. The same may be said of the various colour tests.

In separating the liquid fatty acids, it will be found advantageous to use the zinc instead of the lead soaps. It is probable that the iodine absorption may be found by acting directly on the ethereal

solution of the zinc soap without previously liberating the oleic acid; this would save much time.

The best test at present is the phytosterol test. Enough phytosterol may be obtained from 10 grams of adulterated lard to make a microscopical examination.

L. DE K.

**The Arachidic and Lignoceric Acids of Earth-nut Oil and their Estimation.** By LEONARD ARCHBUTT (*J. Soc. Chem. Ind.*, 1898, 17, 1124—1126).—The mean molecular weight of the mixture of acids obtained from earth-nut oil by Renard's process (this Journ., 1872, 180) indicates that it is a mixture of arachidic and lignoceric acids, in which the latter largely predominates. The author modifies Renard's process by precipitating only a fraction of the fatty acids as lead salts; one gram of lead acetate is sufficient to convert the whole of the arachidic and lignoceric acids in 10 grams of earth-nut oil into lead soaps, and there is a great advantage in having less lead oleate to remove by ether. The 10 grams of oil is saponified by 4 grams of sodium hydroxide and 70 c.c. of alcohol; the soap, freed from alcohol, is decomposed by hydrochloric acid, and the fatty acids extracted by ether. After distilling off the ether, the acids are dissolved in 50 c.c. of 90 per cent. alcohol, and the warm solution is precipitated with 5 c.c. of a 20 per cent. solution of lead acetate. The precipitate is digested and washed with ether until free from lead oleate, then decomposed by hydrochloric acid in presence of ether, and the ethereal solution, after washing, is evaporated to dryness, and the residue, dissolved in 50 c.c. of hot 90 per cent. alcohol, is allowed to crystallise for 1 hour at exactly 15°. The crystals are collected on a Gooch filter, washed as prescribed by Renard (see also Tortelli and Ruggieri (Abstr., 1898, ii, 653) and weighed. The author confirms the statement of Tortelli and Ruggieri (*J. Soc. Chem. Ind.*, 1898, 876) that the correction to be applied for the solubility of the mixed acids in 90 per cent. alcohol is greater than was stated by Renard, and agrees with them that the correction must be varied according to the weight of the crystals ultimately obtained. A table for this purpose is given.

M. J. S.

**Estimation of Earth-nut Oil in Admixture with other Oils.** By FERDINAND JEAN (*Chem. Centr.*, 1898, ii, 585; from *Ann. Chim. Anal. Applic.*, 3, 220—221).—Ten grams of the sample to be tested for earth-nut oil is heated to 110°, 3 grams of potassium hydroxide dissolved in spirits of wine added, and the whole well stirred. The soap is then boiled in a reflux apparatus with 100 c.c. of 36 per cent. alcohol, previously saturated at 15° with potassium arachidate, until the mass is entirely dissolved. After being kept for 12 hours at 15°, the alcohol is drained off and the residue treated as before with 100 c.c. of the same alcohol. After removing the liquid portion, the solid soap is dissolved in 50 c.c. of hot water containing a little hydrochloric acid, and the liberated arachidic acid dissolved in light petroleum and recovered by evaporation. Its melting point should be 71—72°; 5.5 parts of arachidic acid represent 100 parts of earth-nut oil.

L. DE K.

**The Constants of Curcas Oil.**—By LEONARD ARCHBUTT (*J. Soc. Chem. Ind.*, 1898, 17, 1009—1010).—An undescribed sample of oil examined by the author was identified as Curcas oil. Its constants, in the crude state (*a*) and refined condition (*b*), as well as those of an undoubted sample of the refined oil (*c*), differed somewhat from those hitherto published.

	<i>a.</i>	<i>b.</i>	<i>c.</i>
Specific gravity at 15.5° .....	0.9205	0.9205	0.9205
Absolute viscosity at 15.5° .....	0.858	0.878	0.864
Rise of temperature with 97 per cent. sulphuric acid (Maumené value) .....	67.5°	66.6°	65.0°
Saponification value (per cent.) .....	19.28	19.25	19.26
Iodine value .....	98.0	99.5	98.8
Hehner value .....	...	95.2	...
Acetyl value (Lewkowitsch) .....	14.03	9.82	8.36
Reichert-Meißl value .....	...	0.28	0.48
Acidity (as oleic acid) (per cent.) .....	11.8	0.36	4.46
Unsaponifiable matter (per cent.) .....	...	0.56	...
Melting point of fatty acids .....	...	27.5°	...

The crude oil was yellowish-brown in colour; the refined oil pale yellow. All three samples saponified readily. Sample *b* solidified at 2.8°. When exposed in a thin film on glass at 50°, sample *b* dried in about 24 hours, sample *c* in 30 hours. With nitric acid of sp. gr. = 1.375, sample *b* gave a pale brown colour, changing to orange after a time. The reactions with silver nitrate (Milliau), and with amylic alcohol, carbon bisulphide, and sulphur (Halphen) were negative.

M. J. S.

**Estimation of Nicotine in Tobacco.** By RUDOLF HEFELMANN (*Chem. Centr.*, 1898, ii, 562—563; from *Pharm. Centr.-Halle*, 39, 523—524).—The author states that he has for two years estimated nicotine in tobacco by a process similar to that described by Keller (this vol., ii, 193). Twenty grams of the sample, dried at 50°, or in a desiccator, is treated in a 300 c.c. glass-stoppered flask with 20 c.c. of 6 per cent. alcoholic potash until the powder is thoroughly moistened, 200 c.c. of ether is added, and the mixture well shaken and left to settle. Fifty c.c. of the ether is now pipetted off and allowed to evaporate in a porcelain dish; the crude nicotine remaining is dissolved in 10 c.c. of alcohol, and, after adding 50 c.c. of water, is titrated with *N*/10 sulphuric acid, using cochineal or hæmatoxylin as indicator. If a more accurate estimation is desired, 50 c.c. of the ethereal extract is distilled off, and the residue, after adding a few drops of aqueous soda and 10 c.c. of water, is distilled in a current of steam, when the distillate may be accurately titrated.

L. DE K.

**Separation and Estimation of Caffeine and Theobromine.** By HEINRICH BRUNNER and HEINRICH LEINS (*Chem. Centr.*, 1898, ii, 512—513; from *Schweitz. Wochschr. Pharm.*, 36, 301—303).—The authors propose the following method for the detection and estimation of caffeine and theobromine in such products as coffee, cocoa, kola, &c.: 10 grams of the powdered substance is boiled for half an hour with 500 c.c. of water, the evaporated water being replaced from time to time. Small quantities of lead hydroxide are now added until the



liquid is colourless, the boiling is continued for another 15 minutes, the liquid filtered, and the residue extracted twice more with 500 c.c. of water; the mixed filtrate is boiled down to 500 c.c., and the lead removed by a current of carbonic anhydride. The filtrate, evaporated to dryness at  $100^{\circ}$  along with some clean sand, is extracted in a Soxhlet apparatus for 6 to 8 hours with ether. The residue left on evaporating the extract to dryness is extracted thrice with 50 c.c. of boiling water; after cooling to  $50^{\circ}$ , the liquid is filtered, evaporated nearly to dryness, and the residue dried at  $80^{\circ}$ . To separate the alkaloids, they are dissolved in hot water, silver nitrate is added, the precipitate dissolved in 2 to 3 c.c. of ammonia, and heated on the water-bath in the dark until the odour of ammonia has disappeared. When cooled to  $30^{\circ}$ , the silver theobromine ( $C_7H_7AgN_4O_2$ ) is collected on a weighed filter and dried at  $100^{\circ}$ . The silver in the filtrate is precipitated with sodium chloride, the filtrate evaporated to dryness, and the caffeine extracted with ether. The alkaloid is dried at  $100^{\circ}$  and weighed.

L. DE K.

**Separation of Creatine.** By E. F. LADD and P. B. BOTTENFIELD (*Amer. Chem. J.*, 1898, 20, 869—871).—Neubauer's method for the separation of creatine gives somewhat higher values than the methods of Stradeler or Liebig. In Liebig's process, it is impossible to remove the last traces of barium by means of carbonic anhydride without a slight loss of creatine, whilst the use of alcohol in Stradeler's method involves the extraction of fatty material, in subsequently removing which a loss of creatine always occurs, although the error here is not so great as that in Liebig's method.

W. A. D.

**Comparison of Methods for Estimating Caffeine.** By E. F. LADD (*Amer. Chem. J.*, 1898, 20, 866—869).—The values obtained by the methods of Vite, Peligot, and Crosshoff are always lower than those obtained by Gomberg's process (*Abstr.*, 1897, i, 129), which is at once the most accurate and most simple. Vite's method appears to be entirely untrustworthy.

W. A. D.

**Behaviour of Prussian Blue with Solvents in the Presence of Fat.** By WILHELM FRESENIUS and LEO GRÜNHUT (*Zeit. anal. Chem.*, 1899, 38, 31—33).—During the examination of a blue transfer paper for coal-tar dyes, the observation was made that Prussian blue ground with oil (what oil is not specified) yields, on treatment with either ether or chloroform, a clear blue solution, which can be filtered unchanged. When ground with oleic acid, the solutions were still more deeply coloured. With light petroleum, on the contrary, a perfectly colourless solution of the oil was obtained.

M. J. S.

**Estimation of Indigo-blue and Indigo-red in Natural and Synthetical Indigo.** By W. F. KOPPESCHAAR (*Zeit. anal. Chem.*, 1899, 38, 1—10).—The older methods of estimating indigotin are untrustworthy when applied to the product obtained by the methods in use at the present day for the manufacture of natural indigo, as this contains far more indigo-red than was formerly the case. The author gives the preference to a colorimetric method, on the ground of its directness and rapidity; it is,

however, essential to remove at least the greater part of the indigo-red and indigo-brown, by digestion with glacial acetic acid in which both these colouring matters are soluble. Half a gram of the finely pulverised indigo is mixed with 100 c.c. of glacial acetic acid in a conical flask, and heated in the water-bath at  $100^{\circ}$  for an hour with frequent shaking; after allowing the undissolved substances to subside completely (the flask being left in an oblique position for an hour), the clear solution is carefully decanted through a filter of ignited asbestos, and if from the depth of colour of the solution the proportion of indigo-red seems to be considerable, the residue is again washed with glacial acetic acid. The residue in the flask and the asbestos filter are now treated with 50 c.c. of pure concentrated sulphuric acid and kept at  $70^{\circ}$  for 2 hours, the small quantity of acetic acid (about 6 c.c.) left in the flask being found to have no prejudicial influence. The solution is then diluted to 250 c.c. and 25 c.c. of this is again made up to 500 c.c. and is colorimetrically compared with a solution containing 0.1 gram of pure indigotin per litre. A special colorimeter based upon that of Salleron (this Journal, 1872, 527) is figured and described. For the estimation of the indigo-red, an aliquot part of the acetic acid extract is partially (about  $\frac{3}{4}$ ) neutralised with sodium hydroxide, whereon the indigo-red is precipitated whilst the indigo-brown remains in solution. The precipitate is collected on a small filter and washed with a 5 per cent. sodium hydroxide solution and finally with water containing 2 per cent. of acetic acid, dried, dissolved in 50 c.c. of glacial acetic acid and compared colorimetrically with pure solution of indigo-red in glacial acetic acid (50 milligrams per litre). The latter may be conveniently prepared by diluting with water a glacial acetic acid extract of a suitable indigo, washing the precipitate with sodium hydroxide, and subliming it under reduced pressure. The synthetical indigo red introduced into commerce by the Badische Anilin und Soda Fabrik is not identical with the natural substance, and is not free from indigotin. Like all colorimetric processes, the method requires acuteness of vision; in the author's case, the errors varied between 0.2 and 0.8 per cent. for indigo-blue, and for indigo-red were even smaller.

M. J. S.

**Estimation of Urinary Indican.** By FRITZ OBERMAYER (*Zeit. physiol. Chem.*, 1899, 26, 427—428).—Wang (Abstr., 1898, ii, 659) has described a method of estimating the indican in urine which is, in principle, the same as the author's (*Wiener klin. Rundschau*, 1898, No. 34). In some details, however, the methods differ, and these are commented upon.

W. D. H.

**Some Reactions of Biliary Acids and their Detection in Urine.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1898, ii, 1035; from *Boll. Chim. Farm.*, 37, 609—617).—When biliary acids are slowly heated in a dish with concentrated sulphuric acid, the liquid turns first yellow, then orange yellow, and finally blood red. If the heat is raised until white fumes are visible, the liquid afterwards shows a green fluorescence; this can be observed even when the colours are not very plain owing to interfering matters. If biliary acids are moistened with sulphuric acid and then covered with hydrochloric

acid, green streaks are noticed which turn blue, violet, and finally red. To isolate the acids from urine, the latter, after being acidified and concentrated, is mixed with chloroform and sufficient alcohol to dissolve this; on adding water, the chloroform (containing alcohol) separates and contains the biliary acids. Amylic alcohol also extracts the acids. To test for the acids in the presence of biliary colouring matters, the author decolorises the urine with freshly precipitated lead sulphide, and then tests for the acids in the filtrate.

L. DE K.

#### Detection of Albumin and Albumoses in Animal Liquids.

By E. RIEGLER (*Zeit. anal. Chem.*, 1899, 38, 68; from *Pharm. Centr.*, 1897, 379).—A solution containing albumin, even at a dilution of 1:40000, gives with  $\beta$ -naphthalenesulphonic acid a precipitate insoluble on heating. Albumoses are also precipitated by this reagent, but the precipitate dissolves on heating, and reappears on cooling. Aluminium  $\beta$ -naphtholdisulphonate (so-called alumnol) in acid solutions is also a serviceable reagent. The author uses a solution containing 4 grams of alumnol and citric acid in 100 c.c., and adds 20—30 drops to 10 c.c. of the liquid to be tested. With this reagent also, the albumose precipitate dissolves on warming.

M. J. S.

Estimation of the Bitter Principles in Hops. By CARL J. LINTNER (*Chem. Centr.*, 1898, ii, 684—685; from *Zeit. Ges. Brauw.*, 21, 407—410).—The process recommended by the author is not intended as a commercial one for the valuation of hops, but promises to become of scientific interest. Into a 500 c.c. flask having also a mark at 505, 10 grams of the sample is introduced; 300 c.c. of light petroleum is added, and the flask is attached to a reflux condenser. The flask is heated by inserting it to the depth of 2—3 cm. in water at about 50°; it is important that the boiling point of the solvent should be between 30° and 50°. The bulk of the bitter principle is dissolved after about 2 hours, but the boiling is continued for 8 hours; when cold, the liquid is made up to the top mark at 17.5°, well shaken, and at once filtered. One hundred c.c. of the filtrate is mixed with 80 c.c. of commercial absolute alcohol, phenolphthalein is added, and the liquid is titrated with *N*/10 alcoholic potash containing as little water as possible. A blank experiment should be made to ascertain the amount of potash neutralised by the mixture of alcohol and light petroleum. The amount of alkali required by the sample multiplied by 0.4 represents the bitter principle (chiefly lupulin). Hops generally yield from 14.6—12.7 per cent. by this process.

L. DE K.

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## General and Physical Chemistry.

**Influence of Elements on the Optical Activity of the Amyl Radicle.** By A. BRJUCHONENKO (*J. pr. Chem.*, 1899, [ii], 59, 45—52).—When sulphur is introduced into the molecule of amyl compounds in direct combination with the amyl group, the specific rotation is largely increased. If either amylic sulphide or bisulphide is dissolved in carbon bisulphide, and sulphur is added to the solution, the specific rotation is not increased by the uncombined sulphur.

	AyOH.	AySH.	AySMe.	AySEt.	Ay <sub>2</sub> S.	Ay <sub>2</sub> S <sub>2</sub> .	AyI.
$[\alpha]_D$	-4.34°	+2.20°	+12.30°	+13.75°			
	-4.40				+24.52°		+4.15°
	-4.30					+72.48°	

It is found that when elements of the same group of the periodic system are attached to the amyl radicle, they increase the specific rotation the more, the greater their atomic weights. Further, the influence increases from the 7th to the 5th group. The following table gives the values of the specific rotations, divided by two when two amyl groups are present; the amylic ether cited is isoamylic *l*-amylic ether.

NHAy <sub>2</sub> = +2.80°	Ay <sub>2</sub> O = + 0.70°	AyCl* = +1.24°.
	Ay <sub>2</sub> S = +12.26	AyBr* = +3.50.
	Ay <sub>2</sub> Se = +20 (?)	AyI* = +5.41.

\* These were prepared from a sample of alcohol which had  $[\alpha]_D = -5.7^\circ$ , the others from a sample with  $[\alpha]_D = -4.4^\circ$ , to which correspond AyBr  $[\alpha]_D = +2.51^\circ$  and AyI  $[\alpha]_D = +4.17^\circ$ ,  $[\text{Ay} = \text{C}_5\text{H}_{11}]$ .

C. F. B.

**Relation between Structural and Magneto-optic Rotation.** By A. W. WRIGHT and D. ALBERT KREIDER (*Amer. Journ. Sci.*, 1898, [iv], 6, 416—427).—It seemed possible that if an inactive compound, capable of forming active crystals, were allowed to crystallise in a magnetic field, one of the active forms might predominate, or that the field might in other ways influence the formation of active products. Experiments were first made with dextrotartaric acid, 5 grams of which, with 3 c.c. of water, were heated (1) under ordinary conditions, (2) in a strong magnetic field, but no difference was observable between the final products. Sodium chlorate was then allowed to crystallise in a magnetic field, and although the first set of experiments appeared to indicate an excess of dextro-crystals, further experiments proved that this was purely accidental, a field of 800 C.G.S. units having no effect on the crystals, although a tendency of the crystals to cluster in the strongest part of the field was observed both with sodium chlorate and with ferrous sulphate. Owing to the negative nature of these results, the authors repeated Kipping and Pope's researches on the crystallisation of sodium chlorate in dextrose solutions (*Trans.*, 1896, 606), but without their definite results.

L. M. J.

NOTE BY ABTRACTOR.—The authors only refer to the abstract of Kipping and Pope's paper which appeared in the *Chemical News*, and VOL. LXXVI. ii.

appear to be familiar only with this, as they state erroneously that "Kipping and Pope do not state the number of results upon which they have based their conclusions." The difference is perhaps ascribable to the fact that the authors employed a 5 per cent. solution of dextrose, whereas Kipping and Pope used a 20 per cent. solution.

**Spectra of Hydrogen.** By THEODORE W. RICHARDS (*Amer. Chem. J.*, 1899, 21, 172—174. Compare Abstr., 1897, ii, 199).—Hydrogen containing a trace of water vapour readily gives the red four-line spectrum when submitted to the continuous discharge, whereas the perfectly dry gas gives the "white spectrum," and a very great strength of current must be employed to obtain the red spectrum under these conditions. The heterogeneous water molecule more readily undergoes dissociation, and the red spectrum is characteristic of atomic hydrogen; the homogeneous hydrogen molecule is more stable, and the white spectrum is due to molecular hydrogen. G. T. M.

**Anomalous Dispersion of Incandescent Sodium Vapour.** By HENRI BECQUEREL (*Compt. rend.*, 1899, 128, 145—151).—The author has continued his investigations of the anomalous dispersion of incandescent sodium vapour (*Compt. rend.*, 1898, 127, 899), and has recognised that two different anomalous dispersions due to  $D_1$  and  $D_2$  respectively are superposed, the superposition being most distinct between the two lines, and in this interval there is an extraordinarily rapid variation in the index of refraction with a change in wave-length. For rays very near  $D_1$  or  $D_2$  but of somewhat shorter wave-length, the index of refraction is less than unity. It is noteworthy that, in this region, the vapour is at one and the same time absorbing and emitting rays of the same wave-length, and it would seem that this peculiar state of motion is the cause of the perturbations observed. The author's observations are in accord with the theory of anomalous dispersion propounded by Lord Kelvin and Helmholtz.

When the prismatic flame containing the incandescent sodium vapour is placed in a powerful magnetic field, the phenomena observed are due to a superposition of the anomalous dispersion and Zeeman's phenomenon. For a given wave-length, the vibrations parallel with the field have not the same index of refraction as the vibrations perpendicular to the field, and it follows that the vapour should be birefractive, as suggested by Voigt, who first observed the phenomenon. C. H. B.

**Chemical Effects of X-Rays.** By P. VILLARD (*Compt. rend.*, 1899, 128, 237—239).—When photographic plates that have been exposed to the action of X-rays are afterwards exposed to light, the image undergoes reversal in the same way as if both exposures had been made to light, and the precise character of the phenomena depends on the relative magnitudes of the exposures. Plates exposed for some time to X-rays show increased sensitiveness to the less refrangible rays. C. H. B.

**Electrosynthesis.** By WILLIAM G. MIXTER (*Amer. J. Sci.*, 1898, [iv], 6, 217—224. Compare Abstr., 1898, ii, 202).—The action of the electric glow discharge on different gaseous mixtures has been further studied.

The view previously expressed, that the heat resulting from the combination effected by the feeble glow discharge does not cause further combination, is confirmed. The use of a solution of potassium hydroxide, in place of the solid, does not influence the rate of change produced by the current through hydrogen and oxygen. It has been proved that, in the case of hydrogen and oxygen, the greater the pressure, the more rapid is the combination.

A mixture of ammonia and oxygen undergoes decomposition, about five-sixths of the nitrogen being liberated as such, whilst the remainder goes to form a deposit of ammonium nitrite on the side of the tube. Methylamine is oxidised more slowly than hydrogen and a certain amount of nitrite is formed; dimethylamine behaves in a similar manner, but trimethylamine does not yield nitrous acid. A mixture of aniline vapour and of oxygen at  $30^{\circ}$  under a pressure of 100 mm. contracts very slowly indeed, a brown condensation product being formed, but no nitrous acid. A mixture of dry cyanogen (1 vol.) and oxygen (2 vols.) first increases a little and then slowly contracts to about its original volume, and a considerable amount of carbonic anhydride, but no nitrous acid, is produced. When nitrous oxide itself is subjected to the glow discharge, complicated changes slowly occur, nitrite, and probably nitrate, being formed in the presence of potassium hydroxide. A mixture of nitrous oxide and hydrogen yields nitrogen and water. Nitric oxide, in the presence of potassium hydroxide, yields higher oxides when subjected to the glow discharge, and a mixture of nitric oxide and hydrogen reacts in a similar manner, but more slowly, nitrite being produced. A mixture of nitric and carbonic oxides yields but little carbonic anhydride. J. J. S.

**Electro-chemical and Thermo-chemical Properties of Zinc and Cadmium Amalgams.** By THEODORE W. RICHARDS and G. N. LEWIS (*Zeit. physikal. Chem.*, 1899, 28, 1—12).—As the thermal capacity of an amalgam is approximately equal to the sum of the thermal capacities of the components, the heat of amalgamation is practically constant, and hence also the temperature coefficient of the E.M.F. must be constant, being given by the expression,  $E/T - Q/ne_0$ ; the E.M.F. should, therefore, be a linear function of the temperature. The E.M.F.'s of cells of zinc and cadmium amalgams of various concentrations, and of amalgams against pure metal were determined, and it was found that, except in the case of the highest concentrations, the E.M.F. was in accord with the value calculated by the usual expression, and that  $E/T$  was constant and not affected by the nature of the anion. The heat of amalgamation of cadmium was found to be 505 cals., and that of zinc -2255 cals. The contact E.M.F. between the pure metal and amalgam was also determined, and was only appreciable in the case of cadmium amalgam, for which it reached about 0.05 volt.

L. M. J.

**Alteration of Free Energy in Melted Halogen Compounds of some Heavy Metals.** By VINCENT CZEPIŃSKI (*Zeit. anorg. Chem.*, 1899, 19, 208—282).—In any chemical system, the changes in free energy,  $E$ , and total energy,  $Q$ , are connected by the relation  $E = Q + T \cdot dE/dT$ , where  $T$  is the absolute temperature. In the electrolysis of a fused electrolyte, the alteration of free energy,  $E$ , is easily obtained

from the E.M.F. of polarisation, and the total energy,  $Q$ , from the heat of formation of the compound. The above expression hence becomes  $n \cdot 23041 \cdot \epsilon = Q + T \cdot d\epsilon/dT \cdot n \cdot 23041$ , where  $\epsilon$  is the E.M.F. of polarisation,  $n$  the valency of the reacting substances, and 23041 the factor, for conversion into Calories. From measurements, therefore, of the E.M.F. and temperature coefficient, the heat of formation may be calculated. The salts were melted in V-tubes of hard glass contained in a sand mantle in a gas furnace, the temperatures being taken with a Le Chatelier pyrometer; electrodes of carbon, one reaching to the bend, the other to the surface of the molten salt, were employed, and the polarisation was compared with that of a Clark cell by the aid of a ballistic galvanometer. Zinc chloride was first examined, and it was found that by electrolysis the salt could be obtained perfectly anhydrous, no metal being deposited for some time, during which the polarisation increased; when the salt is anhydrous, the polarisation becomes constant and metal is formed; it is noteworthy that the salt is a better conductor when anhydrous than when slightly hydrated. The polarisation was also determined by the direct measurement of the E.M.F. of the chain  $C | Zn | ZnCl_2 | Cl | C$ , the gas electrode being obtained by the use of a carbon wick. The polarisation varied from 1.5765 volts at  $408^\circ$  to 1.2089 volts at  $728^\circ$ ; the temperature coefficient was almost constant, being 0.00075 up to  $600^\circ$ ; above this, it appeared to decrease, but the values are not trustworthy. From the numbers, the heat of formation is found to be 95.86 Cal. at  $408^\circ$  and 96.1 Cal. at  $468^\circ$ ; the value found by Thomsen was 97.2 Cal. at  $18^\circ$ , which leads to the values 95.9 Cal. and 97.59 Cal. at the above temperatures, neglecting, however, the latent heat of fusion of the salt. From the difference between the heat of formation, just above and below the melting point, the molecular heat of fusion of zinc is calculated as 1.94 Cal., a result in accord with the actual value 1.83 Cal. Similar values for the other salts investigated are contained in the accompanying table, in which the column  $Q^1$  contains the values for the heat of formation deduced from Thomsen's and Berthelot's observations at lower tempera-

Salt.	Temperature.	$\epsilon$ (in volts).	$-d\epsilon/dt$ .	$Q$ .	$Q^1$ .
Zinc bromide ...	$390^\circ$	1.3342	0.0006	80.1	
" " ...	560	1.1849	0.001		
Lead chloride...	466	1.2714	0.0008	84.7	82.8
" " ...	706	1.096	0.0009	92.3	
Lead bromide...	389	1.1114	0.0007	72.2	71.9
" " ...	700	0.8532	0.00097	89.5	
Lead iodide.....	405	0.6943	0.00067	51.6	44.3*
" " ...	700	0.4842	0.00069		
Silver chloride.	460	0.9106	0.00039	26.8	about 27
" " ...	720	0.8258	0.00053		
Silver bromide..	440	0.8129	0.00044	25.2	25.2
" " ...	680	0.6961	0.00066		
Silver iodide ...	320	0.6189	0.00045	19.2	17.9
" " ...	740	0.4948	0.00020		

\* Polarisation value probably high owing to difficulty of obtaining lead iodide perfectly free from oxygen.

tures. The values here given are the extremes of the trustworthy results, but numerous intermediate values are given in the paper.

A number of molecular latent heats of fusion were calculated as in the case of zinc chloride, namely, silver iodide, 1·573 Cal.; lead bromide, 3·578 Cal.; and lead chloride, 4·13 Cal. The E.M.F.'s of the cells  $\text{Zn} \mid \text{ZnCl}_2 \mid \text{PbCl}_2 \mid \text{Pb}$  and  $\text{Zn} \mid \text{ZnBr}_2 \mid \text{PbBr}_2 \mid \text{Pb}$ , were also determined, the values agreeing well with the differences between the E.M.F.'s of polarisation of the two salts. Comparison of the complete results shows that the temperature coefficients of the halogen compounds of a metal differ but little, that of the bromide being the greatest, and that of the iodide least, a result in accord with the conclusions of Bodländer (Abstr., 1897, ii, 554). L. M. J.

**Alteration of Free Energy in Molten Halogen Compounds of some Heavy Metals.** By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1899, 19, 283—290).—It was shown by Czepinski (preceding abstract) that the E.M.F. of the chain  $\text{Zn} \mid \text{ZnCl}_2 \mid \text{PbCl}_2 \mid \text{Pb}$  is equal to the difference between the E.M.F.'s of the two chains,  $\text{Zn} \mid \text{ZnCl}_2 \mid \text{Cl}$  and  $\text{Pb} \mid \text{PbCl}_2 \mid \text{Cl}$ , and the same obtains for similar bromide cells, the E.M.F. in both cases being almost independent of temperature. It hence follows that the ion pressure is approximately equal in melted lead and zinc chlorides, and in lead and zinc bromides. In Czepinski's experiments, the temperature coefficient remained approximately constant for a considerable range of temperature, and from the mean value for this range the heat of formation of each compound is calculated. If the reactions be represented thus,  $\text{Ag} + \text{Cl} \rightleftharpoons \text{AgCl}$ , &c., then the free energy is given by the expression,  $RT \{ \log C_1 C_2 / C + \log c / c_1 c_2 \}$ , where  $C_1 C_2 C$  are actual and  $c_1 c_2 c$  the equilibrium concentrations of the three components; if  $c / c_1 c_2 = K$ , then  $d \log K / dT = -Q / RT$ , so that the ratios of  $K$  at various temperatures are calculable. For zinc, lead, and silver chlorides, and silver and lead bromides, it is found that the value of  $K$  decreases considerably with rise of temperature, that is, the quantity of undecomposed salt, in the equilibrium state, decreases with rise of temperature. L. M. J.

**Latent Heats of Vaporisation of Liquids.** By WLADIMIR F. LUGININ (*Ann. Chim. Phys.*, 1898, [vii], 13, 289—377).—In order to determine the latent heats of vaporisation, it was first necessary to obtain the specific heats of the liquids examined between their boiling points and ordinary temperatures, and also to determine the variation of boiling point with pressure; the methods and results of this preliminary work are fully described. The following liquids were examined: ethylic, propylic, isopropylic, butylic, isobutylic, active amylic, fermentation amylic, allylic, and benzylic alcohols; amylene hydrate, ethylenic glycol, methyl ethyl ketone, methyl isopropyl ketone, diethyl ketone, methyl butyl ketone, dipropyl ketone, methyl hexyl ketone, mesityl oxide, benzaldehyde, ethylic oxalate, ethylic carbonate, methylic carbonate, acetal, decane, octane, and benzene. They were all purified as completely as possible, and in many cases had an absolutely constant boiling point. The specific heats were determined by the method of mixtures, and it is noteworthy that, in spite of the extreme care observed, the values obtained with the same



specimen frequently differed by over 1 per cent. The latent heats of vaporisation were determined in the usual manner, and results were obtained agreeing to within 1 per cent., a mean of four determinations being usually employed. In the case of the alcohols examined, the latent heat was found to decrease with increase of molecular weight, and the values differ for isomerides, that of the normal compound being the greater. For ethylic, isopropylic, butylic, isobutylic, and allylic alcohols, and ethylenic glycol, the values  $MS/T$  ( $T$ =absolute boiling point) have a practically constant value of about 26.1 to 26.5, the three amylic alcohols give a lower value (about 25), whilst for benzylic alcohol the value is only 22.9. For the ketones studied,  $MS/T$  is markedly less than for the alcohols, the mean value being 20.83, with extremes of 21.29 and 20.57; the values given by benzaldehyde and mesityl oxide also agree with these ketonic values. The ethereal salts give values slightly greater than those of the ketones, the mean being 21.79, whilst the hydrocarbons examined gave numbers approximating to 20. It appears, therefore, that Trouton's law,  $MS/T=k$ , is approximately valid, but that the value of  $k$  varies somewhat with different series of compounds, being abnormally great in the case of the alcohols. The abnormal value is probably due to complex groups which have been proved to exist in alcohols, and in this series also, it is most marked for those compounds in which, according to Ramsay and Shields, the greatest complexity occurs. The magnitude of the expression  $MS/T$  may thus serve as a means of recognising the existence of liquid complexes, the normal value being taken as about 20 to 21. The heats of combustion of the compounds examined are only known for the liquid state, but by adding the values found for the latent heats, the heats of combustion for the gaseous state may be obtained. The correction, in general, amounts to about 2 or 3 per cent., and the values so corrected are given (compare Abstr., 1896, ii, 146).

L. M. J.

**Specific Volumes and Thermodynamic Relations of Steam: Regnault's Calorie.** By G. P. STARKWEATHER (*Amer. Jour. Sci.*, 1899, [iv], 7, 13—33; 129—142).—The work involves chiefly a careful reinvestigation of Regnault's calculations of the latent and total heat of steam. The temperatures are shown to have been reduced to the air thermometer, and the chief error in the determinations to be due to the assumption of a constant specific heat of water. Corrections are made employing the expression  $h = 1.00449t - 0.0_31904t^2 + 0.0_51813t^3$  for the total heat of water, and it is proved that the correction gives values for the latent and total heats of steam more concordant than the values calculated by Regnault's formulæ; and an expression,  $H = 603.2 + 0.356t - 0.0021t^2$ , is proved to furnish better values for the total heat of steam above 100° than does Regnault's linear formula. For temperatures below 100°, the expression  $598 + 0.442t - 0.0_364t^2$  is in accord with Dieterici's and Regnault's experiments. The values for the specific volumes of saturated steam may be calculated from the latent heat, and many experimental determinations of these and of the volumes of superheated steam have been made by Battelli, and by Ramsay and Young, but the author comes to the conclusion that the discrepancies in these determinations are irreconcilable, and hence

that our knowledge of the specific volumes of steam is limited to the saturation point. The 'equation of condition' connecting temperature, pressure, and volume is investigated, that finally adopted being  $p = RT(v - a) - A/Tv^{3/2}(v^{\frac{1}{2}} + \gamma)$ , and the necessary constants are given. A table is finally given for the values of the total heat, latent heat, pressure, volume, entropy of water, entropy of dry steam, and energy of dry steam at temperatures up to  $200^{\circ}$ , the heat being in terms of the specific heat of water at  $15^{\circ}$ .  
L. M. J.

**Heat Developed on Adding Water to Excess of Sulphuric Acid.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 13, 77).—The amounts of heat developed on successively adding equal quantities of water (1–4 mols.) to excess of sulphuric acid (20 mols.) are as follows:—1st,  $H_2O = +7.5$  Cal.; 2nd,  $H_2O = +7.26$  Cal.; 3rd,  $H_2O = +7.07$  Cal.; 4th,  $H_2O = +6.93$  Cal.

G. T. M.

**New Method for the Determination of the Melting Points of Fats.** By HENRY R. LE SUEUR and ARTHUR W. CROSSLEY (*J. Soc. Chem. Ind.*, 1898, 17, 988).—Into a small, thin-walled tube, a fine capillary tube open at both ends is placed. The diameter of the capillary should not be more than 0.75 mm. A small portion of the substance is introduced into the bottom of the outer tube, so that the end of the capillary is well surrounded by it, the tube is then attached to a thermometer and heated in the usual manner, the temperature at which the liquid is seen to rise in the capillary being taken as the true melting point. The method is accurate, and the observed melting point is not influenced by the position of the capillary in the wider tube.

J. J. S.

**Stannic Bromide as a Solvent in Cryoscopic Determinations.** By FELICE GARELLI (*Gazzetta*, 1898, 28, ii, 253–261).—The author finds that stannic bromide is sometimes useful as a solvent in the determination of molecular weights by the freezing point method; it offers the advantage of having a very high molecular depression, and further, it melts at a temperature (about  $30^{\circ}$ ) very convenient in practice.

Benzene and acetophenone turn stannic bromide yellow, but many other organic substances, especially halogenated derivatives, dissolve in it without change.

A number of determinations with solutions of different substances points to a mean value of 280 for the molecular depression of freezing point.

Stannic chloride and iodide, when dissolved in stannic bromide, produce molecular depressions greater than the theoretical value, showing that they do not form solid solutions; in connection with this, it is pointed out that stannic bromide and iodide are not isomorphous.

T. H. P.

**Apparatus for Determining the Specific Gravity of Pulverulent Substances.** By GUSTAV J. W. BREMER (*Rec. Trav. Chim.*, 1898, 17, 405–406).—The author has recently described (this vol., ii, 81) an apparatus for measuring the density of pulverulent substances, but was not at that time aware of the papers of Paalzow (*Ann. Phys.*

*Chem.*, 1881, [ii], 13, 222, and 14, 176) and Baumhauer (*Arch. Néerl.*, 1868, 385), in which volumeters are described similar to the author's in general principle. He believes, however, that his own apparatus possesses the following advantages over all others: (1) The volume of the flask can be chosen in accordance with the volume of the substance to be contained in it. (2) The increase in volume for the diminution of pressure can be regulated so that the effect is a maximum.

A. L.

**Tables for Correction of Temperature in Pyknetric Measurements.** By PAUL FUCHS (*Zeit. angew. Chem.*, 1899, 25—27).—The author prefers taking the capacity of sp. gr. bottles by filling them with water at the temperature of the laboratory; this, however, necessitates several corrections. To facilitate the work, he has constructed four tables. The first one gives the increase in volume of sp. gr. bottles when the temperature rises from 4° to 30°; the second, the expansion of water between these temperatures; the third, the capacity of the specific gravity bottle at 4° when the water used has a temperature between 4° and 30°; whilst the fourth table serves to calculate  $d_{15^\circ/15^\circ}$  to  $d_{15^\circ/4^\circ}$ .

Examples are given showing the way of using the tables.

L. DE K.

**Viscosity of Undercooled Liquids.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1899, 28, 17—32).—Viscosity is commonly regarded as the criterion of the solid or liquid state, but the author points out that undercooled liquids have a viscosity approaching that of crystals, whilst some crystals have a viscosity approaching that of liquids, with a definite change at the melting point (*Abstr.*, 1898, ii, 563). There is, further, no discontinuity in the change from a liquid to an amorphous solid, and the latter may hence be regarded as an undercooled liquid. In order to determine whether any discontinuity in the viscosity occurs during the undercooling of liquids, the author made determinations of the viscosity at various temperatures reaching far below the melting point in the case of the following substances:—piperine,  $\alpha$ -naphthyl salicylate,  $\beta$ -naphthyl salicylate, peucedanin, cocaine, papaverine, cane sugar, leucine, and glucose. The method first employed was that used by Jones (*Phil. Mag.*, 1894, 37, 451) namely, the measurement of the time of fall of a heavy sphere through the liquid, but afterwards a more speedy method was found to consist in the observation of the velocity with which a glass filament was drawn out of the liquid by a constant force. In no case was any discontinuity found in the viscosity | temperature curve, and measurement usually became impossible at from 100° to 50° of undercooling. The expansion curve of  $\beta$ -naphthyl salicylate was also found to be perfectly continuous up to temperatures at which the compound is quite hard, so that the change from liquid to amorphous solid is quite continuous.

L. M. J.

**Velocity of Crystallisation.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1899, 28, 96—98).—A final reply to Küster (this vol., ii, 15), in which the author upholds his contention that the temperature of the freezing point prevails in the limiting layer of an undercooled liquid during solidification.

L. M. J.

**Change of Entropy in the Dissociation of similar Heterogeneous Systems.** By CAMILLE MATIGNON (*Compt. rend.*, 1899, 128, 103—104).—When comparable chemical systems, such as the compounds of metallic chlorides with ammonia, undergo heterogeneous dissociation, the heats of formation of the compounds from the products of dissociation are proportional to the absolute temperatures corresponding with the same dissociation pressure. In the case of the ammoniacal chlorides of zinc, calcium, silver, magnesium, palladium, and lithium, the quotient  $Q/T$  (where  $Q$  is the heat of formation of quantities of the compounds that liberate the same amount of ammonia, and  $T$  is the absolute temperature at which the dissociation pressure is equal to the atmospheric pressure in each case), is practically constant and varies only from 0.31 to 0.337, although the value of  $T$  varies from  $285^{\circ}$  to  $453^{\circ}$ . Since  $Q/T$  represents the change of entropy corresponding with a reversible chemical change at atmospheric pressure, it follows that when similar systems dissociate with the same dissociation pressure, the change in entropy is the same in all the systems. C. H. B.

**The Theory of Osmotic Pressure.** By K. SCHREBER (*Zeit. physikal. Chem.*, 1899, 28, 79—95).—If two similar aqueous solution, of an electrolyte be separated by a semipermeable membrane which allows the passage of only one ion, then each side is subject to an equal osmotic pressure, but if an electric current passed through the liquid in a direction at right angles to the plane of the division, then one side of the division experiences an increase of pressures analogous to a wind pressure, owing to the increased velocity of the ions in the direction of the current. A copper ferrocyanide membrane is impermeable to copper, zinc, and  $\text{SO}_4^{2-}$  ions, but permeable to potassium and  $\text{NO}_3^{-}$  ions. In the solutions of copper or zinc nitrate, an increase of pressure was found on the side opposed to the anode; in solutions of potassium sulphate on that opposed to the cathode; whilst in solutions of copper sulphate no increase of pressure occurs—results which are in accord with the theory. The author deduces, on the basis of the kinetic theory as applied to solutions, an expression for the magnitude of this 'ion-wind pressure,' which should be proportional to the E.M.F. and to the partial pressure of the ion. Experiments showed that in any particular cell the pressure is actually proportional to the E.M.F., but it was found that the ratio  $dP/dE$  varied to a very great extent (in ratio 1:76) when different cells were used, and as this variation is inexplicable theoretically, and as the actual values are not of the same order of magnitude as those calculated, the author considers that the kinetic theory cannot be applied to solutions. L. M. J.

**Osmotic Pressure of Ethereal Solutions.** By H. M. GOODWIN and GEORGE K. BURGERS (*Zeit. physikal. Chem.*, 1899, 28, 99—114).—Noyes and Abbot have shown that the osmotic pressure of ethereal solutions of naphthalene and azobenzene is approximately proportional to the concentration, that is, Boyle's law is obeyed in these solutions (*Abstr.*, 1897, ii, 395). Whilst, however, the numbers in the case of azobenzene are approximately constant, yet, for the naphthalene solutions, the ratio  $P/C$  decreases with increase of concentration, and

the variation is too great to be referred to experimental errors. The authors, therefore, again investigated the question, and determined the vapour pressure of ether and of various solutions by the dynamical method, temperatures being taken by a platinum resistance thermometer. The compounds employed were diphenylamine, naphthalene, and benzophenone and in each case the ratio  $P/C$  was found to decrease with increase of concentration, that is,  $PV$  decreases with increase of pressure as in the case of easily compressible gases. For diphenylamine, the curve of  $PV$  against  $P$  appeared to indicate that a minimum exists, after which the value again increases, exhibiting a further analogy to the gas laws. Azobenzene is, therefore, the only compound examined for which the simple law is applicable.

L. M. J.

**Cause of Osmotic Pressure.** By F. BARMWATER (*Zeit. physikal. Chem.*, 1899, 28, 115—144).—The author endeavours to prove that the various phenomena depending on osmotic pressure may be explained on the assumption that this is due to an attraction between the molecules of the solvent and the solute, and do not necessitate the supposition that the molecules of the latter move freely as in the gaseous state. On this hypothesis he deduces the van't Hoff expression  $PV = RT$ , and shows that Abegg's cryoscopic observations on aqueous and benzene solutions are in accord with his theory. In the case of dissociated compounds, he deduces the dilution formula  $\mu_{\infty} = \mu + g \sqrt[3]{\mu/v}$ , and shows that, in the case of solutions of potassium and sodium chlorides, this expression gives results which are at least as closely in accord with the experimental values as those obtained by the use of Kohlrausch's formula. The values of  $\mu$  and  $g$  are given for a large number of salts, and the expressions deduced are applied to find the osmotic pressure and dissociation of some salt solutions, the results being concordant.

L. M. J.

**Solubility of Acids in Solutions of the Salts of other Acids.** By ARTHUR A. NOYES and EDWARD S. CHAPIN (*J. Amer. Chem. Soc.*, 1898, 20, 751—756; and *Zeit. physikal. Chem.*, 27, 442—446).—Determinations of the solubility of benzoic acid in solutions of sodium acetate and sodium formate, at various concentrations, were made, and the values found were compared with those calculated by the aid of the expressions deduced by Noyes (this vol., ii, 9). The agreement was very close, as shown by the following numbers, which are the values for the highest concentrations.

Sodium acetate.			Sodium formate.		
Concentration of salt.	Sol. calc.	Sol. found.	Concentration.	Sol. calc.	Sol. found.
0.00000	0.02793		0.0090	0.02793	
0.05282	0.06380	0.06480	0.05657	0.04553	0.04530

L. M. J.

**Reaction between Potassium Permanganate and Hydrochloric Acid under the Influence of Catalytic Agents.** By JULIUS WAGNER (*Zeit. physikal. Chem.*, 1899, 28, 33—78).—In the estimation of ferrous salts by potassium permanganate, the presence of hydrogen chloride necessitates the use of excess of the permanganate owing to this reacting with the acid and evolving chlorine. The author investigated this reaction especially in regard to the action of various salts as catalytic agents. Sulphates have usually a retarding influence, and this is very marked in the case of aluminium sulphate, probably owing to the slight dissociation of aluminium chloride, and the consequent removal of chlorine ions; other salts, such as the acetates, were also found to retard the reaction. Chlorides, however, usually cause an increase in the quantity of permanganate required, that is, have an accelerating effect; barium chloride has a very marked action and also causes oxidation of oxalic acid by permanganate in the cold; the action in this case is probably due to the intermediate formation of a peroxide. The chlorides of platinum, chromium, and cadmium have also a marked action on the permanganate, the quantity of the latter required for the oxidation of a definite quantity of oxalate being greater than when hydrochloric acid of equal chlorine concentration is added. The action of platinic chloride was further examined, and is most probably due to the formation of hydrogen platinochloride, which reacts with the permanganate more readily than hydrogen chloride itself. Electromotive force determinations also show that this compound has the lower decomposition point. It is probable that the activity of the chlorides of chromium, gold, and cadmium is also due to the formation of an acid chloride; indications of the presence of a compound of this kind in the case of cadmium chloride are given both by the E.M.F. determinations and by cryoscopic experiments. The author suggests that cases such as these, in which the acceleration is due to secondary reactions, should be distinguished by the term 'pseudo-catalysis.'

L. M. J.

**Velocity of Inversion in Aqueous Alcohol.** By ERNST COHEN (*Zeit. physikal. Chem.*, 1899, 28, 145—153).—The author has previously shown that the dissociation of electrolytes, as measured by the conductivity, is equal in aqueous alcohol and in pure water (*Abstr.*, 1898, ii, 154). The velocity of inversion of cane sugar is, however, diminished by the addition of alcohol, and this was, therefore, examined further. Hydrogen chloride was employed as hydrolyst, and it was found that the ratio of the velocities in water and in 50 per cent. alcohol was independent of the concentration of the sugar, but increased with the dilution of the acid, reaching a constant value of 1.5 at about  $N/32$ . In 20 per cent. alcohol, the constant ratio is much smaller, about 1.05, and is already reached at the concentration  $N/8$ . As at very high dilution the dissociation is complete in both solvents, it follows that the difference in the velocities is not due to dissociation differences, but to a specific action on the velocity of reaction of the medium in which the reaction takes place.

L. M. J.

**Dynamical Researches on the Formation of Azo-compounds. III.** By HEINRICH GOLDSCHMIDT and EMIL BÜCKLE (*Ber.*, 1899, 32, 355—378. Compare *Abstr.*, 1897, i, 278; 1898, ii, 20).—The relation between the velocity of formation of azo-compounds, formed from diazobenzenesulphonic acid and tertiary amines, and the strength of the acid used, is shown in the following table.

The expression  $k_{\text{HCl}} = kx$  indicates that the velocity of formation is the same when other acids of the same strength are used in place of hydrochloric acid, the hydrolytic constant  $x$ , for weaker acids, being dependent only on the dissociation constant of the acid, and not on its constitution, therefore the constant of velocity,  $ks = kx/k' = k_{\text{HCl}}/k'$ , where  $k'$  is the dissociation constant of the acid.

Acid.	Base.	$\delta$ .	$k_{\text{HCl}}$ .	$100k'$ .	$\frac{k_{\text{HCl}}}{k'}$ .	$ks$ Found.
Chloracetic acid.....	Diethylaniline ...	25°	0·00145	0·155	0·94	1·15
Acetic acid .....	„ .....	25	0·00145	0·0018	80·6	77·7
„ .....	„ .....	20	0·00095	0·0018	52·8	49·2
Formic acid .....	Dimethylaniline.	20	0·00053	0·0214	25·0	25·8
„ .....	Diethylaniline ...	20	0·00095	0·0214	4·4	3·9
Propionic acid .....	„ .....	20	0·00095	0·00134	70·9	61·0
„ .....	„ .....	25	0·00145	0·00134	108·2	108·7
Levulinic acid .....	„ .....	20	0·00085	0·0025	37·3	38·3
„ .....	„ .....	25	0·00145	0·0025	57·0	75·3
Lactic acid .....	„ .....	20	0·00095	0·0310	3·1	3·1
„ .....	„ .....	25	0·00145	0·0310	4·7	5·0

From the consideration of numerous other instances of the velocity of formation of azo-compounds from diazonium salts, &c., the assumption made by the authors in the case of the formation of amidoazo-compounds, namely, that that part only of the tertiary amine which is set free by the hydrolysis of the salt combines as such with the diazo-compound, appears to be proved.  
J. F. T.

**Solubility and Melting Point as Criteria for Racemic Compounds, Pseudoracemic Mixtures, and Inactive Conglomerates.** By H. W. BAKHUIS ROOZEBOOM (*Ber.*, 1899, 32, 537—541).—Racemic compounds, pseudoracemic mixtures, and inactive conglomerates can be readily distinguished the one from the other by determining either the curve of solution at constant temperature, or the melting point curve of the solid, or the solidifying curve of the liquid substance.

In this way, the racemic nature, or otherwise, of a substance having the same or a lower melting point than its active constituents can be definitely determined. The term inactive conglomerate is considered to best express a mere mixture of the active constituents. The subject will be discussed in detail in a forthcoming paper in the *Zeit. physikal. Chem.*  
J. F. T.

**What is a Chemical Individual?** By F. WALD (*Zeit. physikal. Chem.*, 1899, 28, 13—16).—Tammann has shown that the water content of certain hydrated salts varies continuously (this vol., ii, 8),

and the author, considering that this throws doubt on the accepted atomistic laws of definite and multiple proportions, again reviews the question as to what is a chemical individual, with reference to his definition deduced on the basis of phase law (*Abstr.*, 1898, ii, 159).

L. M. J.

**Filtration.** By JEAN HAUSSE (Compt. rend., 1899, 128, 112—114).—The author has investigated the rate of passage of water and alcohol through finely divided kaolin, calcium phosphate, and animal charcoal in uniform layers of different thicknesses and under different pressures. The rate of flow is constant for the same liquid and the same filtering medium, and is inversely proportional to the thickness of the layer of one and the same substance. Other conditions being constant, the rate of flow diminishes as the pressure is reduced and increases as the pressure is increased up to a certain point, beyond which it becomes independent of the pressure.

Crystalline filtering media yield different and less uniform results.

C. H. B.

**Filtration of Organic Liquids.** By JEAN HAUSSE (Compt. rend., 1899, 128, 242—243. Compare preceding abstract).—The author has made experiments on the filtration of various typical carbon compounds through layers of kaolin, animal charcoal, and calcium phosphate. The filtering layer is not affected by the passage of successive quantities of different liquids, that is to say, the respective rates of filtration are not affected if different liquids are passed through a given filtering layer one after the other in any order. The relative rates of filtration of different liquids are independent of the nature of the filtering material. By adjusting the thicknesses of the three filtering materials, it is possible to prepare filters that are equivalent whatever the nature of the liquids. For equivalent filters and for a given pressure, each liquid has its own coefficient of filtration. These conclusions hold good also for solutions of carbon compounds in alcohol of 90°, but they do not hold good for aqueous solutions.

C. H. B.

**Filtering small quantities of Liquid.** By HENRY VON WINKLER (*Chem. Zeit.*, 1898, ii, 1066).—When filtering a few c.c. of liquid, it often happens that the solution does not readily pass through the filter and partly evaporates. The apparatus devised by the author consists essentially of a glass plate of which one side is ground and having at its centre a projecting tube fitted to a rubber tube. A funnel with ground edges is fitted with strong paper and filled with the liquid; the disc, which may also be made of vulcanite, is placed on the top of it, and held in position with the fingers while the liquid is forced through the filter by blowing air through the tube.

L. DE K.

**A New Separating Funnel.** By GEORG W. A. KAHLBAUM (*Ber.*, 1899, 32, 509—510).—The author describes a novel form of separating funnel in which the tap is superseded. The escape tube fits closely into a ground-glass conical jacket, on the inner surface of which a



groove has been cut for a portion of its length on one side. In one position, the groove makes a continuous channel with the escape tube, but on rotating the jacket, communication is interrupted.

M. O. F.

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## Inorganic Chemistry.

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**Metallic Halogen Salts.** By VICTOR THOMAS (*Ann. Chim. Phys.*, 1898 [vii], 13, 145—231. Compare Abstr., 1895, ii, 271, 450, 495; 1896, ii, 26, 365, 429, 527, 608, 609; 1897, ii, 145, 262, 377; 1898, ii, 585).—A detailed account of work already published. G. T. M.

**Constitution of Inorganic Compounds. XV. Chloro-salts.** By ALFRED WERNER (*Zeit. anorg. Chem.*, 1899, 19, 158—178).—A review of all the known chloro-salts shows that those chlorides which act as anhydrides of chloro-acids are, as regards their power of forming salts, analogous to the oxygen acids, that is, that the reactions expressed in the following equations,  $K_2O + SO_3 = K_2O \cdot SO_3$  and  $KCl + AuCl_3 = KCl \cdot AuCl_3$ , are analogous, and the products of both reactions are salts of the second order. Some of the anhydrides of chloro-acids enter into reaction as simple molecules: for instance, copper chloride, manganese chloride, and platinum chloride; others show a tendency to act as polymeric acid anhydrides in a somewhat similar manner to chromium and tungsten trioxides: for example, lead, gold, and mercury chlorides. The trivalent elements show this tendency in a marked degree; the quadrivalent elements do not. The same chloro-compound can give rise to different definite acids in a similar manner to that in which the anhydrides of oxygen acids do. Thus, as phosphoric anhydride yields different acids according to the different degrees of hydration, so, in a similar manner, cadmium chloride is able to form salts with 1, 2, or 4 molecules of an alkali chloride. The limit is always reached when the number of chlorine atoms in the acid radicle becomes six. In the case of hydrated chloro-salts, also, the sum of the chlorine atoms and water molecules is never greater than six.

E. C. R.

**Relation of Hypochlorites to Chlorates.** By FRITZ FOERSTER and F. YORRE (*J. pr. Chem.*, 1899, [ii], 59, 53—101).—The reaction of chlorine with the solution of an alkali hydroxide is usually described as follows. In cold, dilute solutions, hypochlorite and chloride are formed; in hot, concentrated solution, chlorate and chloride are obtained. Such statements completely ignore the work of Gay Lussac, who pointed out long ago (*Compt. rend.*, 1842, 14, 927, or *Annalen*, 43, 153) that the conversion of hypochlorite to chlorate does not so much require a high temperature and a concentrated solution, as the absence of alkalinity, obtained by saturating the solution with chlorine.

The authors have investigated the matter anew. They passed

chlorine gas (prepared by electrolysis with platinum electrodes, and consequently free from carbonic anhydride) into a freshly prepared solution of sodium hydroxide of about 25 per cent. strength, the containing vessel being immersed in cold water and shaded from light; when prepared, the hypochlorite solution was allowed to remain in the dark, at the ordinary or at some other temperature. From time to time, samples were removed, and the available oxygen was estimated: that in the hypochlorite with arsenite solution, and the total amount by distillation with concentrated hydrochloric acid, the distillate being collected in potassium iodide solution, and the iodine which was liberated, titrated. Dissolved chlorine gas was first removed by aspirating air through the solution. By making estimations at intervals while the chlorine was being passed in, the extent to which the alkali was saturated could be ascertained; complete saturation was attained when the total available oxygen corresponded with that theoretically obtainable with the amount of sodium hydroxide employed.

If the alkali solution is not quite saturated with chlorine, the slightly alkaline hypochlorite solution formed is very stable at the ordinary temperature; after 4 weeks, only 14 per cent. of the hypochlorite had been converted into chlorate, but at the same time a small quantity of oxygen gas had been evolved. In daylight, the conversion is somewhat more rapid, and the same is the case at 50°, whilst at 90°, 67 per cent. was converted in 2 hours; the more rapid conversion, however, was attended by a greater loss owing to evolution of gas, and this loss is greater the more alkali is present. If a slight excess of chlorine is present above the amount required to saturate the alkali, the conversion is very rapid at the ordinary temperature; after some 2 hours, 93 per cent. of the hypochlorite was converted into chlorate, and the loss corresponded with but a fraction of a per cent. If the text-book method is adopted, and concentrated caustic soda is saturated at 90–95° with chlorine, 88·5 of the theoretical yield of chlorate is obtained, but there is a loss of 10·5 per cent. A rapid, and almost equally complete conversion, is attained by adding a small quantity of an acid; sulphuric, phosphoric and acetic acids and sodium hydrogen carbonate were experimented with, and it was found that the extent of the conversion did not vary much, but that its rate varied with the amount of the hydrogen ions added, that is, with the amount of hypochlorous acid set free. Increased concentration of the hypochlorite and a higher temperature also promote the conversion.

Hypochlorous acid is but extremely little dissociated in solution, and it is the undissociated molecule of this acid that, in the author's opinion, oxidises the hypochlorite to chlorate. The acid itself undergoes but a very slow change in aqueous solution, in the absence of other substances; if a hypochlorite is added, a rapid formation of chlorate occurs. Now the hypochlorite solution contains hypochlorite ions, and it is to a reaction between these and undissociated hypochlorous acid that the formation of the chlorate is attributed:

$$2\text{HOCl} + \text{ClO}^- = 2\text{H}^+ + 2\text{Cl}^- + \text{ClO}_3^-; \text{ or } \text{HOCl} + 2\text{ClO}^- = \text{H}^+ + \text{Cl}^- + \text{ClO}_3^-.$$

The presence of an alkali chloride promotes the action, but chlorine gas is evolved at the same time ; in this case, chloride ions are oxidised

to chlorate by the hypochlorous acid :  $6\text{HOCl} + \bar{\text{Cl}} = 3\text{HOCl} + 3\text{H}^+ +$

$3\bar{\text{Cl}} + \text{ClO}_3^- = 3\text{H}_2\text{O} + 3\text{Cl}_2 + \text{ClO}_3^-$ . As the hypochlorous acid is used up, it is continuously regenerated from the hypochlorite ions of the alkali hypochlorite and the hydrogen ions of the acid added, or, failing that, of the water. So long, however, as alkali hydroxide is still in excess, abundance of hydroxyl ions are present, and these reduce the concentration of the hydrogen ions of the hypochlorous acid, uniting with them to form water ; to remain in equilibrium with this diminished concentration of hydrogen ions, the concentration of the undissociated hypochlorous acid must decrease too (by dissociation and union of its hydrogen ions with the hydroxyl ions present to form water), and the amount of it that remains undissociated is too little to effect the conversion of hypochlorite into chlorate at any considerable rate. (When a solution of potassium carbonate is chlorinated, it is only after it has become half saturated, that is, after all the carbonate has been converted into hydrogen carbonate, that chlorate is formed at an appreciable rate). But if the base employed is one that yields only a small concentration of hydroxyl ions to the solution, then the concentration of the hydrogen ions is reduced to a much smaller extent, the existence of undissociated hypochlorous acid in much greater concentration is possible, and the conversion of hypochlorite to chlorate can be effected much more rapidly. It was found, in fact, that, when an approximately neutral sodium hypochlorite was mixed in separate portions with magnesium sulphate, calcium chloride, and zinc sulphate in amounts equivalent to the hypochlorite present, conversion of the latter into chlorate took place very slowly in the first case, less slowly in the second, fairly rapidly in the third, whilst, in the first case, no precipitate formed, in the second a slight precipitate of calcium hydroxide formed gradually, and in the third a dense precipitate of zinc hydroxide formed at once. In the case of the electrolysis of a calcium chloride solution, the results are complicated by the fact that the calcium hydroxide separates at the anode in very different conditions ; sometimes it separates in such a form that it redissolves but slowly when the electrolysed solution is allowed to remain ; in this case, a fairly rapid conversion into chlorate ensues. Sometimes only a little separates, and that in such a form that it readily dissolves ; in that case, the hydroxyl ions are maintained at a comparatively high concentration in the solution, and it is found that the conversion into chlorate takes place very slowly. When chlorine is passed into water containing silver oxide in suspension, and the mixture is repeatedly shaken, silver chloride and hypochlorite are formed ; if the shaking is omitted, hydrolysis of the hypochlorite ensues to some extent, and the hypochlorous acid formed, no longer neutralised by being brought continually into contact with silver oxide, effects the conversion of the silver hypochlorite into chlorate, silver chloride being precipitated.

In the case of mercuric oxide, the mercuric hypochlorite is probably hydrolysed very largely, forming undissociated hypochlorous acid; at the same time, most of the mercuric chloride which is formed is withdrawn from the solution in the form of the insoluble oxychloride, and the small amount that remains dissolved is, as is well known, dissociated to but a slight extent. The solution, therefore, is comparatively deficient in both hypochlorite and chlorine ions, there is little that the undissociated hypochlorous acid can oxidise to chlorate ions, and as is found in fact, very little chlorate is formed, the reaction being the usual method of preparing hypochlorous acid.

The hypochlorous acid used was obtained by passing chlorine into water containing freshly prepared yellow mercuric oxide in suspension, and well shaken, the vessel being immersed in water and kept in the dark. Only a trace of chlorate was formed, and the solution contained 4.8 per cent. HOCl; on distillation, about half decomposed, yielding chloric acid and chlorine, but the first fifth that passed over contained as much as 8.5 per cent. HOCl.

C. F. B.

**Experiments on High Strength Hypochlorite Solutions.** By MAX MUSPRATT and E. SHRAPNELL SMITH (*J. Soc. Chem. Ind.*, 1898, 17, 1096—1100. Compare Abstr., 1897, ii, 206).—In order that strong solutions of hypochlorite may be obtained by passing chlorine into sodium hydroxide solution, the following conditions must be adhered to. (1) An excess of alkali must always be present. (2) The temperature must be kept as low as possible, and should not rise above 27°. (3) The solution at starting should be of such sp. gr. as to allow the sodium chloride to settle rapidly. (4) The formation of scum must be avoided; if formed, it should be removed. (5) To obtain higher strengths than those corresponding with the amount of alkali, which experience showed could not be exceeded in the original solutions, solid sodium hydroxide must be added from time to time.

The stability of these solutions was investigated by exposing them in glass cylinders to full daylight during the summer months. The results indicate that the presence of iron in a hypochlorite has a serious influence on its stability, for it is converted into sodium ferrate which reacts with the hypochlorite, causing, not only the evolution of oxygen, but the formation of a considerable amount of chlorate. In the absence of iron, the hypochlorite is stable up to the point when sodium chloride begins to be deposited, but from that stage to a point where all the salt is deposited, it is not quite so stable, although its stability is considerable; beyond the stage where sodium chloride ceases to be deposited, absolute instability exists. In favourable circumstances, a hypochlorite can be made containing 35 per cent. by volume of available chlorine. During the investigations, crystals of sodium hypochlorite have been obtained; they contained NaOCl, 37.6, NaCl, 3.7, and water, 58.7; per cent. no chlorate was present.

J. J. S.

**Density and Molecular Weight of Ozone.** By ALBERT LADENBURG (*Ber.*, 1899, 32, 221—222).—A reply to the criticisms of Staedel and Gröger (this vol., ii, 150); the author agrees with their conclusion that the molecular weight of ozone cannot be determined by taking

the density of a mixture of ozone and oxygen and also estimating the quantity of iodine which the mixture can set free, but argues that this conclusion has no connection with his work. J. F. T.

**Ozone.** By MARIUS OTTO (*Ann. Chim. Phys.*, 1898, [vii], 13, 77—144. Compare Abstr., 1897, ii, 139 and 207).—The various forms of ozonisers are discussed, and an apparatus described, constructed for use with alternating currents, by means of which 15 per cent. of the theoretical amount of ozone can be produced; the yield obtained from Siemens and Andreoli's ozonisers is less than 2 per cent.

Methane at ordinary temperatures is oxidised by ozone to methylic alcohol, formaldehyde, and formic acid; at 100°, the latter substances alone are obtained. Ethylene, treated with ozonised oxygen containing less than 50 milligrams of ozone per litre, yields acetaldehyde and acetic acid; neither ethylic alcohol nor glycol could be detected among the products of oxidation. Acetylene is decomposed by ozone with explosive violence, and carbon is deposited. Methylic and ethylic alcohols, when treated with ozone, yield small quantities of the corresponding aldehydes and acids. Glycol also gives aldehydic and acidic substances, but the only substance isolated was glyoxal. Glycerol furnishes similar products, but their exact nature could not be determined. The mono- and di-hydric phenols are attacked by ozone, but resinous products are obtained, except in the case of catechol, which gives a small quantity of a substance resembling purpurogallol. Isoeugenol, isosafrole, and anethoil are oxidised to vanillin, piperonal, and anisaldehyde respectively. Aniline is oxidised to quinone and azobenzene, and paratoluidine to parazotoluene.

G. T. M.

**Combustion of Mixtures of Hydrogen and Oxygenated Gases.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 167—170).—When hydrogen, mixed with carbonic anhydride or sulphurous anhydride, is exploded with excess of oxygen, the hydrogen is oxidised to water without affecting either of the other compounds. If a mixture of hydrogen and carbonic anhydride is ignited in a vessel open to the air, a portion of the compound gas is reduced to carbonic oxide; a mixture of hydrogen and sulphurous anhydride similarly treated yields small quantities of hydrogen sulphide and free sulphur. The temperature produced by the combustion of the hydrogen causes dissociation of the oxygenated gas, the carbonic anhydride giving rise to carbonic oxide and oxygen, the sulphurous anhydride to sulphur and oxygen; the oxygen unites with hydrogen, whilst a portion of the sulphur combines with this element to form hydrogen sulphide. These products of combustion, being cooled to a temperature below their ignition point before diffusing into a part of the system containing free oxygen, are found in the residual mixture at the close of the experiment.

G. T. M.

**Action of Hydrogen on Sulphurous Anhydride.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 289—293. Compare preceding abstract).—Hydrogen and sulphurous anhydride, whether dry or moist, have no action on one another at the ordinary tem-

perature ; the dry gases react at a red heat, water and sulphur being produced ; if the temperature is not too high, hydrogen sulphide is also obtained. The paper concludes with a discussion of the nascent state from a thermochemical standpoint. The reaction  $\text{SO}_2 + 3\text{H}_2 = 2\text{H}_2\text{O} + \text{H}_2\text{S}$  is exothermic, but the heat developed is not sufficient to determine the change at the ordinary temperature, but if the heat developed by the action of zinc on dilute sulphurous acid be added, the action takes place even in the cold. G. T. M.

**Action of Sulphuric Acid on Metals.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 176—204).—Hydrogen is evolved when zinc is treated with concentrated sulphuric acid in the cold ; at  $180^\circ$ , hydrogen and sulphurous anhydride are evolved, and zinc sulphate is produced ; there is no formation of zinc sulphide. Free hydrogen reduces concentrated sulphuric acid to sulphurous anhydride (Abstr., 1898, ii, 160), but not to hydrogen sulphide ; the latter gas is produced by the direct action of zinc on moderately concentrated sulphuric acid (78 per cent.) and on sulphurous, hyposulphurous, and polythionic acids ; this action is usually attributed to nascent hydrogen. When treated with cold dilute sulphuric acid, zinc sulphide evolves hydrogen sulphide ; with hot concentrated acid sulphurous anhydride is produced. Hydrogen sulphide is decomposed by sulphuric acid of concentration greater than that corresponding with  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ , the products being sulphur, sulphurous, and polythionic acids. Iron and cadmium are attacked by the concentrated acid in the cold, and hydrogen is evolved, but at  $160^\circ$ , the gas generated consists chiefly of sulphurous anhydride. Nickel is only very slowly attacked by cold concentrated sulphuric acid, owing to the formation of a protective layer of sulphide. Sulphurous acid acts on these metals, forming the sulphides and sulphur.

Lead is not acted on by dilute sulphuric acid in the cold, and only slightly at  $100^\circ$  ; with the concentrated acid, the reaction is very slow, owing to the deposition of sulphate and sulphide. If dilute sulphuric acid be distilled in the presence of lead so that its concentration gradually increases, hydrogen sulphide is evolved, and sulphur and lead sulphide are produced. Lead sulphide is decomposed by the concentrated acid, hydrogen sulphide and sulphurous anhydride being successively evolved ; with 60 per cent. acid, the formation of the latter gas is not noticeable. Lead is only superficially blackened by the action of sulphurous acid, and is not attacked by formic and acetic acids. An account of the action of sulphuric acid on mercury has already appeared (Abstr., 1898, ii, 164). Silver, left in contact with the cold concentrated acid for two months, is slightly blackened ; at  $100^\circ$ , sulphurous anhydride is evolved. Silver sulphide is only attacked by the concentrated acid at high temperatures, sulphurous anhydride being liberated. Copper placed in cold concentrated sulphuric acid produces an evolution of sulphurous anhydride, and the metal becomes coated with a layer of sulphide and sulphate ; a similar result is obtained at  $100^\circ$  ; the dilute acid has no action even at this temperature. Copper, heated at  $160$ — $170^\circ$  with a mixture of equal parts by weight of sulphuric acid and water, dissolves, and sulphurous anhydride is

evolved; the liquid, when poured into cold water, yields a crystalline precipitate, consisting of an unstable, cuprous salt, which is formed at a certain stage in this reaction. Copper placed in sulphurous acid becomes superficially coated with sulphide and a red substance, probably a cuprous compound; the metal appears to be attacked by dilute hydrochloric acid at 100°, although no appreciable volume of gas is evolved.

G. T. M.

**Metathetic Reactions between certain Salts in Solution in Liquid Ammonia.** By EDWARD C. FRANKLIN and C. A. KRAUS (*Amer. Chem. J.*, 1899, 21, 1—8. Compare this vol., ii, 208).—Anhydrous liquid ammonia resembles water in its power of inducing electrolytic dissociation, and of acting as a general solvent. The authors have examined the interaction of various salts in this solvent, and find that salts whose ions can by interchange form compounds insoluble in the medium, do react in this sense. The nitrates of 16 common metals were used to furnish the metallic ions, whilst the acidic ions were supplied in the form of ammonium salts. The experiments were made in vacuum jacketed tubes. Ammonium chloride precipitates most of the metallic radicles as chlorides, those chlorides which, by direct experiment, are found to be least soluble in liquid ammonia being precipitated most rapidly and completely. The bromides are more soluble in this solvent than the chlorides, and are precipitated more slowly; only barium and strontium give immediate precipitates with ammonium iodide. All the metallic radicles, except the alkalis, yield precipitates with ammonium sulphide; in the case of magnesium, the precipitate has a composition corresponding with  $2\text{MgS} \cdot (\text{NH}_4)_2\text{S}$ , combined with 9 or 10 molecules of ammonia of crystallisation. Ammonium chromate gives precipitates with all the metallic radicles, except lithium and sodium, and ammonium borate with all but these two alkalis, together with potassium. The results are summarised in tabular form at the end of the paper.

G. T. M.

**Properties of Liquid Ammonia.** By EDWARD C. FRANKLIN and C. A. KRAUS (*Amer. Chem. J.*, 1899, 21, 8—14).—A discussion of the close analogy existing between water and liquid ammonia. Solutions of salts in the latter solvent conduct the electric current almost as well as their aqueous solutions (Cady, *Abstr.*, 1898, ii, 203), and metathetic reactions of a similar nature occur in both media (see preceding abstract). The specific heat, boiling point, and heat of volatilisation of liquid ammonia are abnormally high, like the corresponding properties of water. The molecular elevation of the boiling point of ammonia is smaller than that of any other solvent; its association constant approaches that of water, and exceeds those of the alcohols. Liquid ammonia differs from water in its inability to dissolve the sulphates and sulphites, the alkali carbonates, phosphates, and oxalates, and the hydroxides of the alkali and alkaline earth metals; in its solvent action on many organic substances, it resembles alcohol; it has no point of maximum density, and solid ammonia is not specifically lighter than the liquid at the freezing point. Its dielectric constant is lower than that of water, and, if Nernst's



hypothesis holds, it indicates that the electrolytic dissociation of salts dissolved in this solvent should be less than in aqueous solutions.

G. T. M.

**Hydroxylamine.** By SIMEON M. TANATAR (*Ber.*, 1899, 32, 241—244).—When a 10 per cent. solution of hydroxylamine hydrochloride or sulphate is saturated with sulphurous anhydride, kept overnight, and then evaporated to dryness on a water-bath, it is converted completely into ammonium sulphate; hydrazine sulphate is not attacked by sulphurous anhydride even on heating at  $100^{\circ}$  in a sealed tube. When hydroxylamine hydrochloride is warmed with phosphorus pentachloride, reaction takes place, and on decomposing the product with water and evaporating, it is found that the hydroxylamine has been converted into ammonium chloride; the author explains the action as due to the formation of  $\text{NH}_2\text{Cl} = \text{NH}, \text{HCl}$ , and then  $3\text{NH} = \text{NH}_3 + \text{N}_2$ . By the action of hydrogen peroxide, hydroxylamine hydrochloride is oxidised directly to nitrogen and nitric acid, and no ammonia is produced; when the oxidation is carried out in presence of sodium hydroxide, the chief product is nitric acid, together with a small amount of nitrogen.

T. M. L.

**Hydroxylamine.** By FRITZ RASCHIG (*Ber.*, 1899, 32, 394).—With regard to Tanatar's explanation of the action of sulphurous anhydride on aqueous hydroxylamine hydrochloride (preceding abstract), the author points out that, in this change, hydroxylamine does not act as an oxidising agent, but simply condenses with the sulphurous anhydride, forming sulphamic acid (compare *Abstr.*, 1887, 549), which subsequently undergoes hydrolysis.

W. A. D.

**Constitution of Hydroxylamine.** By JULIUS W. BRÜHL (*Ber.*, 1899, 32, 507—508).—The author criticises the views of Tanatar regarding the constitution of hydroxylamine (compare preceding abstracts).

M. O. F.

**Heat Developed by the Action of Water on Excess of Nitric Acid.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 207—208).—The heat developed by the successive additions of small quantities of water (1 to 3 mols.) to a considerable excess (31.44 mols.) of nitric acid was determined with the following results: 1st,  $\text{H}_2\text{O} = +4.54$  Cal.; 2nd,  $\text{H}_2\text{O} = +4.55$  Cal.; 3rd,  $\text{H}_2\text{O} = +4.59$  Cal.

G. T. M.

**Action of Aqueous Alcoholic Alkalis on Phosphorus.** By AUGUST MICHAELIS and M. PITSCH (*Ber.*, 1899, 32, 337—339).—Phosphorus gradually dissolves in a mixture of 1 volume of 10 per cent. sodium hydroxide solution and 2 volumes of alcohol with the production of a dark red solution, nearly pure hydrogen being eliminated during the process. If the solution be acidified with dilute hydrochloric acid, a greenish-yellow precipitate is produced which is none other than the phosphorus suboxide,  $\text{P}_4\text{O}$ , first obtained by Le Verrier. The suboxide is insoluble in all solvents except aqueous alcoholic alkali; this solution is not stable, but decomposes when left, or on warming, with evolution of hydrogen phosphide and hydrogen.

J. F. T.

**Metallic Phosphides.** By ALBERT GRANGER (*Ann. Chim. Phys.*, 1898, [vii], 14, 5—90. Compare Abstr., 1892, 410, 1398; 1893, ii, 526; 1895, ii, 392; 1896, ii, 476, 602, 650; 1897, ii, 215, 265, 323, 371, 453; 1898, ii, 474).—This paper contains an historical introduction and an account of work already published. G. T. M.

**Preparation of Arsenic Hydride.** By A. P. SAUNDERS (*Chem. News*, 1899, 79, 66—67).—Powdered arsenic, mixed with a small quantity of freshly-cut pieces of sodium, is gently heated in a porcelain boat resting on a strip of asbestos in a piece of wide combustion tube with the ends loosely plugged; when the glass begins to redden, reaction suddenly takes place, and, if the tube is not broken by the violence of the reaction, it is set aside to cool. The hydrogen arsenide is obtained by treating the sodium arsenide with dilute hydrochloric or sulphuric acid. D. A. L.

**Action of Sulphuric Acid on Carbon at Low Temperatures.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 206—207).—Graphite and wood charcoal are not acted on by concentrated sulphuric acid at the ordinary temperature; at 100°, the former remains unaltered whilst the latter produces a slight evolution of sulphurous and carbonic anhydrides without any appreciable quantity of carbonic oxide. G. T. M.

**Chemical Equilibrium between Hydrogen and the Oxides of Carbon.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 170—176).—Carbonic anhydride, when heated at high temperatures, undergoes partial dissociation into carbonic oxide and oxygen. In the presence of carbon or hydrogen, the oxygen thus liberated is employed in oxidising this element, and further dissociation of carbonic anhydride must take place in order to preserve the equilibrium. Water vapour at a similar temperature also undergoes partial dissociation into its components. When a mixture consisting of carbonic anhydride and hydrogen is raised to a high temperature, the state of equilibrium is established, not between the binary systems ( $\text{CO}_2 + \text{H}_2$ ) and ( $\text{CO} + \text{H}_2\text{O}$ ), but between the more complicated system  $\{(n - \alpha)\text{CO}_2 + \alpha(\text{CO} + \text{O})\}$  resulting from the partial dissociation of carbonic anhydride and that produced by the partial dissociation of steam  $\{(m - \beta)\text{H}_2\text{O} + \beta(\text{H}_2 + \text{O})\}$ , and a further complication results from the dissociation of carbonic oxide which reacts in the following sense,  $\{p\text{CO} = (p - 2)\text{CO} + \text{CO}_2 + \text{C}\}$ . This explanation is based on the observed behaviour of these compounds at high temperatures, each of them dissociating in the manner indicated, independently of the presence of the others. The case of mixtures which are being conveyed from the heated space to a cooler zone, and are thus exposed to rapid changes of temperature, must also be considered, since it so frequently obtains in practice.

It follows from this that the mathematical explanations of these phenomena hitherto proposed are quite inadequate, since they assume the existence of hypothetical systems which are never produced under experimental conditions. G. T. M.

**Decomposition of Carbonic Oxide in presence of Ferric Oxide.** By O. BOUDOUARD (*Compt. rend.*, 1899, 128, 98—101).—When finely divided ferric oxide is heated at  $445^{\circ}$  in sealed tubes with purified and dried carbonic oxide, the decomposition of the latter is a function of the time and of the quantity of ferric oxide present. The quantity of carbonic anhydride formed, increases regularly, and eventually the decomposition is complete. Similar experiments are being made with cobalt and nickel oxides at  $445^{\circ}$  and with all three oxides at higher temperatures. C. H. B.

**Reaction with Carbon Oxysulphide.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 205).—Carbon oxysulphide is slowly decomposed by an acid solution of cuprous chloride in accordance with the equation,  $\text{COS} + 2\text{CuCl} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl} + \text{Cu}_2\text{S}$ . G. T. M.

**A New Gas [Etherion].** By CHARLES F. BRUSH (*J. Amer. Chem. Soc.*, 1898, 20, 899—911).—During experiments on the thermal conductivity of gases at pressures of a few millionths of an atmosphere, the author found that heated glass evolves a gas partially reabsorbed on cooling, which is characterised by an exceedingly high conductivity, probably over 100 times that of hydrogen. As the thermal conductivities appear to be in the ratio of the molecular velocities, and hence in the inverse ratio of the square roots of the densities, the author considers the new gas possesses a density of below 0.0001, compared with hydrogen, and that, owing to its great molecular velocity, it is not confined to the atmosphere, but must extend to interstellar space. The name *etherion* is given to it, or to its lightest constituent, if a mixture. L. M. J.

NOTE.—Sir William Crookes (*Chem. News*, 78, 221) considers it more probable that 'etherion' is water vapour at low pressure than that it is an elementary gas. L. M. J.

**Hydrate of Lithium-bromocuprite.** By N. S. KURNAKOFF and A. A. SEMENTSCHENKO (*Zeit. anorg. Chem.*, 1899, 19, 335—338).—*Lithium-bromocuprite*,  $\text{CuBr}_2 \cdot 2\text{LiBr} + 6\text{H}_2\text{O}$ , obtained by evaporating an aqueous solution of its constituents on the water-bath, crystallises in black, prismatic needles having a bronze lustre; in thin layers, they are reddish-brown by transmitted light. It is extremely hygroscopic, does not easily give up its water of crystallisation, and is not dehydrated by remaining over sulphuric acid. This behaviour, in conjunction with the colour, points to the conclusion that the salt contains the hydrate  $\text{LiBr} + 3\text{H}_2\text{O}$ , as expressed in the formula  $\text{CuBr}_2(\text{LiBr} + 3\text{H}_2\text{O})_2$ .

The blue salt,  $(\text{CuCl}_2 + 2\text{H}_2\text{O})_2 \cdot 2\text{KCl}$ , contains the water combined with the  $\text{CuCl}_2$ , and by substituting bromine for chlorine the anhydrous salt  $\text{CuBr}_2 \cdot \text{KBr}$ , is obtained; this is in accordance with the fact that for copper and other metals of the eighth group of the periodic system, the hydrates of the bromo-salts are less stable than those of the chloro-salts. The same relation holds good for the heat of solution of the haloid salts. The instability of the hydrate of cupric bromide has undoubtedly an effect on the composition of the double salt,  $\text{CuBr}_2 \cdot \text{KBr}$ , which contains no water of crystallisation, and the author points out

that a consideration of the colour and the stability of the hydrates gives an insight into the position of the water in the complex molecule of a haloid double salt as expressed in the formulæ  $\text{CuX}_{2n}(\text{LiX} + n\text{H}_2\text{O})_m$  and  $(\text{CuCl}_2 + 2\text{H}_2\text{O})_2\text{KCl}$ .  
E. C. R.

**Action of Alkali Chlorides on Silver.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1898, [vii], 14, 205—206).—Silver in the form of sheets, when immersed in solutions of the alkali chlorides contained in stoppered vessels, is slowly attacked with the formation of double chlorides, the crystals of which adhere to the surface of the metal. The vessels were protected from bright sunlight and allowed to remain for four years; it was found that the sheet immersed in potassium chloride had preserved its bright surface, whilst that in sodium chloride had become tarnished and was of a deep violet colour.  
G. T. M.

**Solubility of Silver Bromide and Chloride in Sodium Thiosulphate Solutions.** By THEODORE W. RICHARDS and HENRY B. FABER (*Amer. Chem. J.*, 1899, 21, 167—172).—Solutions of sodium thiosulphate of varying strengths are saturated with silver bromide and the amount of silver in solution estimated by means of hydrogen sulphide; the results show that the ratio of the bromide to the thiosulphate increases with increase in the concentration of the thiosulphate. The solubility of silver chloride in a 20 per cent. solution of thiosulphate is less than that of the bromide. The addition of silver bromide to a thiosulphate solution raises its freezing point; this result must be due to a diminution of the total number of molecules present, and appears to favour Barth's conclusion as to the formation of a complex ion; the following double salts:  $\text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O}$  and  $\text{Ag}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$  are known in the solid state. Beyond a certain limit, the addition of bromide produces no further rise in the freezing point.  
G. T. M.

**Calcium Arsenide.** By PAUL LEBEAU (*Compt. rend.*, 1899, 128, 95—98).—Calcium arsenide,  $\text{As}_2\text{Ca}_3$ , identical in composition with that formed by the direct union of its constituents, is obtained by heating 100 parts of calcium arsenate and 31 parts of petroleum coke in a carbon crucible in an electric furnace for two or three minutes, using a current of 950—1000 amperes and 45 volts. It forms a crystalline mass, which is transparent and reddish-brown in small fragments, has a sp. gr. = 2.5 at 15°, and in hardness lies between calcite and glass. It is not affected by dry air or oxygen at the ordinary temperature, but when heated burns brilliantly, especially in oxygen, with formation of the arsenate if the oxygen is in large excess, but with sublimation of arsenious anhydride and even of arsenic if it is not. Sulphur attacks the arsenide at a dull-red heat, but boron and carbon have no action at 1000°; in the electrical furnace, however, carbon rapidly and completely decomposes it. In contact with water, the arsenide is completely converted into hydrogen arsenide and calcium hydroxide, without any liberation of hydrogen or separation of a solid brown arsenide as in the action of water on the arsenide obtained by direct synthesis. Moist air somewhat quickly decomposes the arsenide, and

it is attacked at a dull red heat by hydrogen sulphide, by the gaseous hydracids and various oxidising agents. The arsenide reduces sulphuric acid in the cold, and fuming nitric acid on gently heating; it also decomposes many metallic salts.

C. H. B.

**Action of Calcium Sulphate on Halogen Alkali Salts.** By ALFRED DITTE (*Ann. Chim. Phys.*, 1898, [vii], 14, 294—311).—A detailed account of work already published (*Abstr.*, 1898, ii, 510—511).

G. T. M.

**Constitution of Hydraulic Cements.** By ORAZIO REBUFFAT (*Gazzetta*, 1898, 28, ii, 209—247).—The author summarises recent contributions to the chemistry of hydraulic cements, showing how the conclusions arrived at by different workers are in agreement or otherwise with his own. He has examined seven samples of different cements, determining the proportions of free lime and of calcium silicate and aluminate before and after setting, and his results lead to the following conclusions. After setting, hydraulic cements all have the same qualitative composition, being mixtures of calcium hydroxide, hydrated calcium orthosilicate,  $2(\text{SiO}_2, 2\text{CaO}), \text{H}_2\text{O}$ , and calcium aluminate with small quantities of inert slaggy matter. Besides these, in cements rich in silica, there is doubtless present some non-hydrated calcium metasilicate,  $(\text{SiO}_2, \text{CaO})$ , which reacts on the aluminate, forming double silicates of calcium and aluminium; the production of these double compounds has an important bearing on the great resistance to sea-water possessed by such cements. With regard to their composition before setting, the author divides hydraulic cements into two classes. (1) Hydraulic lime and quick-setting cements, which are of a non-crystalline and compact nature, and result from the mixing of aluminate with calcium orthosilicate and in some cases also with lime. (2) Portland and siliceous cements, consisting of a crystalline compound of  $\text{SiO}_2, \text{CaO}$  with varying proportions of  $\text{CaO}$  and a calcium aluminate. The author is of opinion that the hardening of cements is determined mainly by the hydration of the calcium orthosilicate forming  $2(\text{SiO}_2, 2\text{CaO}) + \text{H}_2\text{O}$ , and incidentally also by the hydration of the calcium aluminate.

T. H. P.

**Displacement of Metals by Magnesium.** By EDWARD G. BRYANT (*Chem. News*, 1899, 79, 75—76).—In hot, cold, weak, or strong zinc sulphate solution, only little more than 50 per cent. of the metallic zinc is displaced by magnesium; gas is evolved, and the precipitate formed consists of zinc, zinc oxide, and magnesium oxide. In lead nitrate, chloride, or acetate, hydrogen is evolved in increasing quantities as reaction progresses, and lead is reduced by the magnesium; in some cases, the lead is not oxidised while covered with the liquid, magnesium being present in excess. Silver is also precipitated from its solution by magnesium with progressive evolution of hydrogen.

D. A. L.

**Red Potassium Copper Chloride.** By MAX GRÖGER (*Zeit. anorg. Chem.*, 1899, 19, 328—331).—Potassium copper chloride,  $\text{KCl}, \text{CuCl}_2$ , is obtained as a red powder by shaking a mixture of

copper chloride, finely powdered potassium chloride, and concentrated hydrochloric acid in a closed vessel, provided that the ratio of potassium chloride to copper chloride does not exceed that required by the above formula. If dilute solutions are employed, the compound is obtained in red needles. It is easily soluble in strong hydrochloric acid, and when hydrochloric acid is used to wash the salt, it extracts the copper chloride in preference to the potassium chloride. On exposure to moist air, the salt rapidly becomes green, and yields a mixture of cupric chloride with the blue salt,  $\text{CuCl}_2 \cdot 2\text{KCl} + 2\text{H}_2\text{O}$ . E. C. R.

**Potable Waters which have flowed through Lead Pipes.** By UBALDO ANTONY (*Gazzetta*, 1898, 28, ii, 135—139. Compare Abstr., 1897, ii, 36).—In continuation of his previous work, the author gives the results of experiments made to determine the action on lead of waters containing magnesium sulphate, magnesium hydrogen carbonate, calcium chloride, sodium hydrogen carbonate, with or without alkali chlorides or sulphates, and under different conditions of aëration. The experimental conditions and the method of determination of the lead are the same as those already described (*loc. cit.*, and Abstr., 1895, ii, 549).

The results are summarised in the following table, to which, for the sake of comparison, are added those of the two former series. The numbers given are grams of lead dissolved in 100 litres of liquid :—

Series.		A.	B.	C.	D.	E.	F.	G.
Non-aërated	1. Alone	8.19	2.45	6.83	3.28	1.77	1.80	1.23
	2. With chlorides.	1.36	2.05	5.46	0.99	1.70	1.70	1.34
	3. With sulphates.	3.41	2.18	4.78	1.32	1.36	1.40	0.95
Aërated	1. Alone	12.98	3.14	6.83	1.65	1.70	1.60	0.34
	2. With chlorides.	2.75	3.41	6.57	1.71	1.16	0.90	0.47
	3. With sulphates.	6.83	3.32	5.87	1.71	1.68	0.80	1.16
Continuously aërated	1. Alone	8.19	2.63	3.41	1.58	0.75	1.15	1.16
	2. With chlorides.	0.68	2.35	3.55	1.25	0.54	0.61	0.95
	3. With sulphates.	2.05	2.05	3.69	0.46	0.51	1.02	1.45
With continuous aëration and passage of carbonic anhydride	1. Alone	4.09	5.70	1.35	0.72	0.75	0.88	0.88
	2. With chlorides.	4.09	3.40	1.50	1.12	1.29	0.68	0.68
	3. With sulphates.	1.84	3.16	1.77	0.99	0.89	0.68	0.81

The column A refers to distilled water; B, to water containing per litre 0.04 gram of  $\text{CaO}$ , as calcium hydrogen carbonate, possessing therefore 4° of temporary hardness; C, to water containing 0.232 gram of  $\text{CaSO}_4$  per litre, that is, with a permanent hardness of 9.5°; D, to water with 0.38 gram of  $\text{MgSO}_4$  per litre, corresponding with 9.5° of permanent hardness; E, to water containing 0.195 gram of  $\text{Mg}(\text{HCO}_3)_2$  per litre, that is, having 4° of temporary hardness; F, to water containing 0.046 gram of  $\text{CaCl}_2$  per litre, and G, to water with 5.4 gram of  $\text{NaHCO}_3$  per litre, corresponding with the quantity present in the waters of Vichy (Hôpital), which are among the most alkaline known.

The author concludes that ordinary drinking waters always dissolve a larger or smaller quantity of lead, and that with temporarily hard waters the proportion of lead is much less than with permanently hard waters; this is doubtless due to the insoluble incrustation formed in the former case.

T. H. P.

**Separation of the Cerite Metals.** By CARL VON SCHÉELE (*Ber.*, 1899, 32, 409—417).—Pure lanthana can be readily obtained from a mixture of the rare earths by converting these into the nitrates, and crystallising the product from water containing sufficient ammonium nitrate to form the double salts of the type  $M(NO_3)_3 + 2NH_4NO_3$ ; after 8 crystallisations, the lanthanum double salt is nearly pure, but contains small quantities of cerium, which can be removed by precipitating the double salt as oxalate, dissolving the latter in nitric acid, and treating the nitrate thus obtained by Debray's method. The separation of praseodymium and neodymium from one another and from the metals usually accompanying them is dealt with at length; for details, the original paper should be consulted.

W. A. D.

**Peroxidation of Cerium in presence of Alkali Carbonates.** By ANDRÉ JOB (*Compt. rend.*, 1899, 128, 178—181).—Ceric salts are more soluble than cerous salts in solutions of alkali carbonates, and the solubility is still further increased if they are peroxidised. If, however, an excess of hydrogen peroxide is added, the solubility is reduced and a precipitate forms, the nature of which has not yet been ascertained. In order to obtain a concentrated solution of cerium peroxide, hydrogen peroxide and ceric ammonium nitrate, in molecular proportion, are added successively to a concentrated aqueous solution of potassium carbonate, and the solution is agitated; a limpid, deep-coloured liquid is thus obtained, and as much as 40 grams of cerium dioxide may be added per litre if 280 grams of alkali carbonate are also present. Potassium hydrogen carbonate may be used in place of the normal carbonate, but then the solubility of the cerium salt is less.

If to the solution prepared in the manner just described, hydrogen peroxide is added in slight excess but not in sufficient quantity to produce a precipitate, and the solution is allowed to remain at the ordinary temperature, it at first loses some oxygen, but is afterwards quite stable, the quantity of available oxygen in it corresponding exactly with that required by the formula  $CeO_3$ .

The oxidising power of the solution can be determined by means of a standard solution of ferrous sodium pyrophosphate, the excess being determined by means of permanganate solution. If a small quantity of potassium hydrogen carbonate is added to the liquid, the appearance of a yellow colour indicates that the ferrous salt is completely oxidised and the oxidation of the cerous salt is beginning; if the addition of permanganate is continued, a change of colour from yellow to brown indicates that peroxidation of the cerium has commenced.

Ceric salts do not absorb oxygen from the air, but if a solution of a cerous salt containing also an alkali carbonate is exposed to the air,

it is first oxidised to a ceric salt and then continues to absorb oxygen up to a limit that depends on the strength of the solution.

C. H. B.

**Atomic Weights of Praseodymium and Neodymium.** By HARRY C. JONES (*Zeit. anorg. Chem.*, 1899, 19, 339—341).—A comparison of the independent results obtained by Brauner (*Proc.*, 1898, 70), by Schéele (*Abstr.*, 1898, ii, 519), and by the author (*Abstr.*, 1898, ii, 429), shows that the atomic weights attributed by Auer von Welsbach to praseodymium and neodymium, 143·6 and 140·8 respectively, should be reversed.

E. C. R.

**Aluminium.** By ALFRED DITTE (*Compt. rend.*, 1899, 128, 195—201).—If a strip of aluminium is partly immersed in a solution of sodium chloride acidified with acetic acid, which is capable of dissolving the metal (this vol., ii, 225), the action is far more rapid at the surface of the liquid than at any other point, because the atmospheric oxygen takes part in the reaction. Other acids may be used instead of acetic acid, with similar results, and even carbonic anhydride is active. If a plate of aluminium is partially immersed in a solution of 30 grams of pure sodium chloride in 1000 c.c. of water, which of itself has no action on aluminium, and air is allowed free access to the surface of the liquid, the metal is somewhat rapidly attacked at that surface and becomes coated with gelatinous aluminium hydroxide in which, after a time, opaque, white spots appear and increase in size. At the same time, the solution becomes alkaline to litmus. The oxygen dissolved in the liquid converts a small quantity of the aluminium into oxide, but since the decomposition of sodium chloride by aluminium oxide would be strongly endothermic, the carbonic anhydride of the air must take part in the change, the reaction  $\text{Al}_2\text{O}_3 + 6\text{NaCl diss.} + 3\text{CO}_2 \text{ diss.} = \text{Al}_2\text{Cl}_6 \text{ diss.} + 3\text{Na}_2\text{CO}_3 \text{ diss.}$  developing +33·1 Cal. The sodium carbonate thus formed is able to attack the aluminium with formation of sodium hydrogen carbonate and sodium aluminate and development of a considerable amount of heat; the aluminate is then decomposed by water into aluminium hydroxide and sodium hydroxide, which can produce further reactions. Part of the aluminium hydroxide, however, gradually changes to the crystallised and insoluble form, and is thus removed from the sphere of action. Carbonic anhydride can also decompose the aluminate with formation of the crystallised hydroxide and sodium carbonate, or, under certain conditions, of a double sodium aluminium carbonate; the latter may be decomposed by the sodium hydroxide present in the liquid and will yield sodium carbonate and crystallised aluminium hydroxide. The general character of the reactions is independent of the proportion of sodium chloride present, but is slower the more dilute the solutions; even the small proportion of the salt present in river waters is sufficient, in conjunction with atmospheric oxygen and carbonic anhydride, to set up progressive action on the aluminium.

With sea water, the reactions are similar, the calcium and magnesium chlorides and the sodium bromide behaving in the same way as sodium chloride.



If a small quantity of water containing a soluble chloride or bromide is allowed to fall on a sheet of aluminium, the metal is attacked in the general manner already described; if the salt is not hygroscopic, the attack ceases when the salt and the products become dry, but if the salt is hygroscopic, like magnesium chloride, or if the atmosphere is very moist, the action will continue until the corrosion extends through even a comparatively thick block of aluminium. C. H. B.

**Constitution of Cobalt, Chromium, and Rhodium Bases.** By SOFUS M. JÖRGENSEN (*Zeit. anorg. Chem.*, 1899, 19, 109—157).—A discussion of the relative merits of the theories propounded by the author and by Werner with regard to the constitution of these compounds. E. C. R.

**Carbides of Iron and other Metals in Metallurgical Products.** By ADOLPHE CARNOT and GOUTAL (*Compt. rend.*, 1899, 128, 207—211).—Treatment of ferrotungsten, ferromanganese, &c., by dilute acids or other solvents in the usual way has enabled the authors to isolate several double carbides in addition to those previously described. From tungsten steel containing 2.0 to 2.2 per cent. of carbon and 6.1 to 7.8 per cent. of tungsten, they obtained the carbide  $\text{Fe}_3\text{C}, \text{WC}$ ; from molybdenum steel containing 1.7 to 2.3 per cent. of carbon, the carbide  $\text{Fe}_3\text{C}, \text{Mo}_2\text{C}$ , previously prepared by Williams in the electric furnace. Ferromanganese containing more than 74 per cent. of manganese yields the carbide  $\text{Fe}_3\text{C}, 4\text{Mn}_3\text{C}$ ; that with 74 to 60 per cent. of manganese yields the carbide  $\text{Fe}_3\text{C}, 2\text{Mn}_3\text{C}$ ; that with 60 to 30 per cent. of manganese the carbide  $2\text{Fe}_3\text{C}, \text{Mn}_3\text{C}$ . The last carbide sometimes crystallises in large plates during the cooling of blocks of the ferromanganese. C. H. B.

**Arsenates of Iron.** By HERMANN METZKE (*Zeit. anorg. Chem.*, 1899, 19, 457—478).—The method employed for the analysis of these compounds is as follows. The arsenic is precipitated from a solution of the iron arsenate, strongly acidified with hydrochloric acid, by hydrogen sulphide under pressure, the precipitate of sulphur and arsenic sulphide is cautiously oxidised with fuming nitric acid at  $50^\circ$ , and the solution evaporated on the water-bath. The residue, dissolved in water and ammonia so that a 2.5 per cent. ammonia solution is obtained, is precipitated with magnesia mixture, absolute alcohol added, and the whole allowed to remain 48 hours. The precipitate is then washed with a mixture of 2.5 per cent. ammonia (250 c.c.), with absolute alcohol (100 c.c.), dissolved in dilute nitric acid, and evaporated to dryness in a porcelain crucible, then heated at  $120^\circ$  and finally to bright redness over a strong burner until a constant weight is obtained. Accurate results are obtained.

Ferric arsenate,  $\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_5$ , is formed under varying conditions by the action of 1 mol. of iron ammonium alum on 2—4 mols. of disodium arsenate. The appearance of the precipitate varies with the proportion of the salts employed; when a small quantity of the arsenate is added to the alum solution, a white precipitate is obtained, whilst on adding the alum solution to the arsenate the precipitate is brownish; when the

two salts are employed in equal proportions, a yellow precipitate is formed. The white precipitate turns yellow and finally brownish when washed with water. According to the conditions under which they are formed, the precipitates contain small quantities of basic or acid ferric arsenates, and always contain small quantities of ammonium and sodium arsenates. In the presence of a large excess either of disodium arsenate or of iron ammonium alum, a mixture is obtained consisting mainly of the basic ferric arsenate,  $3\text{Fe}_2\text{O}_3, 2\text{As}_2\text{O}_5$ . Ferric arsenate, which is a bright yellow powder, insoluble in water, is slowly decomposed by cold water, more quickly by hot water, and is soluble in hydrochloric, sulphuric, nitric, dilute arsenic, and phosphoric acids; the solution in the last two acids decomposes when boiled and diluted. Neutral and acid ferric arsenates are quickly and completely dissolved by concentrated ammonia, yielding a blood-red solution; the basic ferric arsenates, however, are not. Yellow ammoniacal solutions are obtained in the presence of large quantities of disodium arsenate and ammonium chloride. These arsenates are not decomposed by a solution of silver nitrate, are quickly decomposed by solutions of ammonium and sodium acetates, and give the reaction of ferric salts with potassium ferrocyanide and thiocyanate only in strongly acid solutions, and never in ammoniacal solutions. Cold concentrated potassium hydroxide precipitates ferric hydroxide from the neutral ferric arsenate, but only an incomplete decomposition takes place when a hydrochloric acid solution of the arsenate is boiled with potassium hydroxide.

Tetrabasic ferric arsenates,  $4\text{Fe}_2\text{O}_3, 3\text{As}_2\text{O}_5$ , approaching in composition that of pharmacosiderite, but containing varying quantities of water and small quantities of sodium and ammonium salts, are obtained by heating the preceding salt with water in a sealed tube at  $200^\circ$ , by boiling it with a solution of ammonium acetate acidified with acetic acid, and by oxidising with hydrogen peroxide, the white precipitate obtained by adding ferrous sulphate to sodium dihydrogen arsenate in molecular proportions.

Arsenates having a similar composition to scorodite,  $\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_5 + 4\text{H}_2\text{O}$ , and differing from it only in the quantity of water which they contain, are obtained in the following manner:—(1) By heating the acid arsenate,  $\text{Fe}_2\text{O}_3, 3\text{As}_2\text{O}_5 + 17\text{H}_2\text{O}$ , with arsenic acid, water, and hydrogen peroxide in a sealed tube at  $170^\circ$  for 14 days, whereby a compound crystallising with  $1\text{H}_2\text{O}$  in yellowish-green, rhombic forms, and mixed with a small quantity of scorodite, is obtained; (2) by heating normal ferric arsenate in a similar manner, whereby a crystalline powder, with  $2\text{H}_2\text{O}$ , is obtained; (3) by heating ferric arsenate with water and arsenic acid in a sealed tube at  $80^\circ$  for 4 days, and (4) by prolonged evaporation of a solution of ferric arsenate acidified with hydrochloric acid. These salts are not altered by boiling water, sulphuric and nitric acids, are sparingly soluble in dilute, easily so in concentrated, hydrochloric acid, dissolve partially in ammonia giving a blood-red solution, and are completely decomposed by potassium hydroxide.

The *arsenate*,  $2\text{Fe}_2\text{O}_3, 3\text{As}_2\text{O}_5 + 22.5\text{H}_2\text{O}$ , is obtained by dissolving ferric arsenate,  $\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_5$ , in arsenic acid and water and precipitating the filtered solution with alcohol; the white precipitate must be quickly washed with alcohol (98 per cent.) and dried by pressing between

filter paper. It dissolves easily in acids, forming a yellow solution, and in ammonia, a red solution. The white acid compound obtained by the action of sodium hydrogen arsenate on iron ammonium alum is quickly decomposed when washed with water, dilute alcohol, or glycerol; it is not altered, however, by strong alcohol or ether, but these solvents do not wash out the impurities in the mother liquor, so that it cannot be obtained pure.

Ferric ortharsenate,  $\text{Fe}_2\text{O}_3 \cdot 3\text{As}_2\text{O}_5 + 16 \cdot 7\text{H}_2\text{O}$ , is obtained as a white powder by adding dry tetrabasic ferric arsenate to a syrupy solution of arsenic acid and washing the product with alcohol; it is quickly decomposed by water, and dissolves in acid with a yellow, and in ammonia with a red, coloration. E. C. R.

**Hydrated Blue Molybdenum Oxide.** By G. MARCHETTI (*Zeit. anorg. Chem.*, 1899, 19, 391—393).—Molybdenum oxide,  $\text{Mo}_2\text{O}_8 + 5\text{H}_2\text{O}$ , is obtained by dissolving molybdenum in strong aqua regia, and after all the nitric acid has been expelled by evaporating the solution on the water-bath, with the addition of hydrochloric acid, the diluted, filtered solution is reduced by means of an electric current. A dark blue liquid is obtained from which the acid crystallises in lustrous, nearly black, triclinic crystals; it is fairly easily soluble in water, and the solution does not give a precipitate on the addition of ammonium chloride. The cryoscopic determinations show that the molecule is neither split into ions nor polymerised in aqueous solution. E. C. R.

**Hydrate of Titanium Trichloride.** By E. POLIDORI (*Zeit. anorg. Chem.*, 1899, 19, 306—307).—*Titanium trichloride*,  $\text{TiCl}_3 + 6\text{H}_2\text{O}$ , is formed by reducing titanium tetrachloride, dissolved in 30 per cent. hydrochloric acid, by aid of the electric current; the violet solution obtained is filtered through glass wool, cooled with ice and salt, and treated with a current of dry hydrogen chloride until the salt crystallises out. The trichloride is deliquescent, oxidises very slowly in dry, but rapidly in moist air; is slowly oxidised in neutral solution with precipitation of titanium oxychloride, but is much more stable in acid solution. The solutions are energetic reducing agents, and when treated with ammonia, yield black precipitates, which, on exposure to the air, quickly turn blue and finally white. E. C. R.

**Derivatives of the Tetrachlorides of Zirconium, Thorium, and Lead.** By J. MERRITT MATTHEWS (*J. Amer. Chem. Soc.*, 1898, 20, 815—839).—The tetrachlorides of zirconium, thorium, and lead do not combine with nitrosyl chloride, nitric peroxide, sulphur monochloride, phosphorus chlorides, cyanogen, hydrogen cyanide, cyanogen chloride, acetonitrile, or benzonitrile, although the chlorides of titanium and tin combine with most of these compounds (compare Hampe, *Annalen*, 1863, 126, 43, and Baeyer, *Abstr.*, 1875, 452). The three tetrachlorides readily combine with ammonia or amines in much the same way as do the chlorides of silicon, titanium, and tin. The compounds may be obtained by the addition of the

pure anhydrous substances to the solutions of the respective chlorides; the zirconium and thorium derivatives, for the most part, form white, flocculent precipitates; the lead salts, however, are of various colours.

The following table gives a list of the compounds which have been prepared and analysed:—

	With zirconium chloride, mols. amine.	With thorium chloride, mols. amine.	With lead tetrachloride, mols. amine.
Ammonia, with dis- solved chloride.....	8	8	4·2
Ammonia, with solid chloride in the cold	2	6	—
Ammonia, with solid chloride when heated	4	6	—
Methylamine .....	4	4	4
Ethylamine .....	4	4	4
Propylamine.....	4	4	4
Aniline.....	4	4	3
Toluidine .....	4	3	decomp.
Pyridine .....	2	1	2
Quinoline .....	2	1	2
$\beta$ -Naphthylamine.....	2	1	1
Diphenylamine .....	no reaction.	no reaction.	decomp.
Acid amides.....	no reaction.	no reaction.	no reaction.

Nearly all these compounds are stable in the air, the chief exceptions being the pyridine, quinoline, and the lower ammonia compounds of zirconium and thorium. None of them exhibits any sign of crystalline structure. When heated in air, they are decomposed into the hydrochloride of the amine and the dioxide of the metal, with the exception of the lead compounds which form lead dichloride. They are also decomposed by water. J. J. S.

**Derivatives of the Tetrabromides of Zirconium and Thorium.** By J. MERRITT MATTHEWS (*J. Amer. Chem. Soc.*, 1898, 20, 839—843).—The following compounds have been obtained:— $\text{ZrBr}_4 + 4\text{NH}_3$ ,  $\text{ThBr}_4 + 3\text{NH}_3$ ,  $\text{ZrBr}_4 + 4\text{NH}_2\text{Et}$ ,  $\text{ThBr}_4 + 4\text{NH}_2\text{Et}$ ,  $\text{ZrBr}_4 + 4\text{NH}_2\text{Ph}$ ,  $\text{ThBr}_4 + 4\text{NH}_2\text{Ph}$ ,  $\text{ZrBr}_4 + 2\text{C}_5\text{H}_5\text{N}$ ,  $\text{ThBr}_4 + \text{C}_5\text{H}_5\text{N}$ .

The bromides were prepared by Mellis' and Troost and Ouvrard's methods. Owing to the slight solubility of the tetrabromides in any of the usual organic solvents, the reagents were added to the dry salts, and any excess was removed by washing the products with ether.

Attempts to prepare lead tetrabromide were unsuccessful.

J. J. S.

**Preparation of Zirconium Nitrides.** By J. MERRITT MATTHEWS (*J. Amer. Chem. Soc.*, 1898, 20, 843—846).—The compound  $\text{TiCl}_4 \cdot 4\text{NH}_3$ , when heated in a current of ammonia, yields a nitride of titanium,  $\text{Ti}_2\text{N}_4$  (Rose, *Ann. Phys. Chem.*, 1829, 16, 57; Persoz, *Ann. Chim. Phys.*, 1803, 44, 321). The authors find that when the compound  $\text{ZrCl}_4 + 8\text{NH}_3$  is placed in a porcelain boat and heated to redness in a current of nitrogen, a zirconium nitride,  $\text{Zr}_3\text{N}_8$ , is obtained. This,

when heated in a current of hydrogen, gives off ammonia, and leaves metallic zirconium.

A second nitride,  $Zr_2N_3$ , is obtained when zirconium tetrachloride is gradually heated to redness in a current of dry ammonia (compare Mallet, *Amer. J. Sci.*, 1858, [ii], 28, 346). J. J. S.

**Germanium.** By CLEMENS WINKLER (*Ber.*, 1899, 32, 307—308).—The author claims priority over Richter in the discovery of the element germanium. T. M. L.

**Vanadium Compounds of the Type  $VX_3$ .** By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1899, 19, 204—207).—*Vanadium sulphate*,  $VSO_4 \cdot 7H_2O$ , is obtained by reducing a solution of the anhydride in sulphuric acid by means of the electric current. The violet-blue solution, when allowed to evaporate in a vacuum over sulphuric acid, yields monoclinic crystals, which are decomposed on exposure to the air. The *double salt*,  $VSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ , obtained by electrolysis a solution of vanadium, containing ammonium sulphate, crystallises in beautiful, amethyst-blue, monoclinic crystals, and on exposure to the air is not so easily decomposed as the preceding salt. The *double salt*,  $VSO_4 \cdot K_2SO_4 \cdot 6H_2O$ , resembles the ammonium salt. All three salts dissolve in water, forming yellow, or brownish-yellow, solutions, which, in the presence of acid, turn blue. Both the acid and neutral solutions absorb oxygen from the air with great rapidity. E. C. R.

**Vanadium Compounds corresponding with the Sesquioxide.** By AUGUSTO PICCINI and N. BRIZZI (*Zeit. anorg. Chem.*, 1899, 19, 394—404).—Vanadium trichloride and tribromide have been described by Locke and Edwards (*Abstr.*, 1898, ii, 598), who obtained them by dissolving the pure hydroxide in hydrochloric and hydrobromic acids respectively, but they are more easily prepared by reducing a solution of vanadic anhydride in hydrochloric or hydrobromic acid by means of the electric current. The green solution of the trichloride so obtained is cooled with ice and salt, and precipitated by saturating it with hydrogen chloride. Vanadium trichloride, in acid or neutral solution, undergoes no change when kept in a sealed tube in an atmosphere of carbonic anhydride, and the crystalline salt remains unaltered for a considerable time in air kept dry by means of lime. The trichloride corresponds in composition with chromium trichloride, and resembles the violet modification of the latter both in chemical behaviour and when examined by the cryoscopic method. Solutions of vanadium trichloride, tribromide, or tri-iodide, when treated with thallium sulphate, yield a precipitate of thallium haloid, whereby all the halogen is precipitated except the small quantity remaining in solution as thallium haloid. Vanadium tribromide is a green, hygroscopic, crystalline powder, but the aqueous solution is either brown or yellow according to the concentration, whilst the acid solution is green, but quickly becomes blue on exposure to the air. *Vanadium tri-iodide*,  $VI_3 \cdot 6H_2O$ , prepared in a similar manner to the trichloride, crystallises in small, green needles, is very hygroscopic, and on exposure to the air changes into a brown

liquid; in preparing this salt, it is necessary to employ a very concentrated solution saturated with hydriodic acid, and to crystallise it in a mixture of ice and salt in a desiccator over sulphuric acid.

*Ammonium vanadium oxalate*,  $V(C_2O_4)_3(NH_4)_3 \cdot 3H_2O$ , is formed on reducing a solution of vanadic anhydride in oxalic acid by means of the electric current; to the brown solution containing a brown precipitate thus obtained, a solution of ammonium oxalate is added, the mixture warmed on the water-bath until the solution becomes clear, after which it is concentrated in a vacuum; it crystallises in green, monoclinic tablets, is stable when exposed to the air, and is soluble in water but insoluble in alcohol. The aqueous solution is green, has strong reducing properties, and is completely precipitated by ammonium and calcium chloride. The salt becomes anhydrous at  $100^\circ$ , but is not otherwise altered.

*Potassium vanadium oxalate*,  $V(C_2O_4)_3K_3 \cdot 3H_2O$ , obtained in a similar manner to the ammonium salt, crystallises in green, monoclinic crystals like those of the ammonium salt, is soluble in water, but insoluble in alcohol, and is dehydrated at  $100^\circ$ , without decomposing. In preparing the two preceding salts, an excess of oxalic acid must be avoided, as otherwise ammonium or potassium hydrogen oxalate is precipitated.

The vanadium double oxalates are similar in composition and crystalline form to the corresponding chromium salts; they behave, however, like double salts, whereas the chromium salts behave like salts of a complex acid, and the chromium is not precipitated by ammonia, nor the oxalic acid by calcium chloride.

The authors were unable to obtain crystalline salts from a solution of vanadium sesquioxide in potassium tartrate. E. C. R.

**Salts of Pyropervanadic Acid and the Constitution of the Peracid Salts.** By PETR G. MELIKOFF and L. PISSARJEWSKY (*Zeit. anorg. Chem.*, 1899, 19, 405—416).—The ammonium salt,  $(NH_4)_4V_2O_{11}$ , is obtained by dissolving ammonium metavanadate in an aqueous solution of hydrogen peroxide, adding ammonia until the solution acquires a distinct ammoniacal odour, and then precipitating the salt with alcohol. It crystallises in minute, slender, yellow, rhombic prisms, remains undecomposed for some time when dry, then slowly decomposes with evolution of oxygen. When treated with concentrated sulphuric acid, it yields ozonised oxygen, and with dilute acid, hydrogen peroxide. The ratio between the ammonia, active oxygen, and  $V_2O_5 = 4NH_3 : 4O : V_2O_5$ , and since the ammonium pervanadate,  $NH_4VO_5$ , is formed by the action of hydrogen peroxide on ammonium metavanadate (Scheuer, *Zeit. anorg. Chem.*, 16, 284), it is most probable that of the four atoms of active oxygen, two are combined with  $V_2O_5$  and two with the  $4NH_3$ . When the salt is treated with a solution of barium chloride, it yields an insoluble precipitate containing barium and ammonium: with silver nitrate, it yields an insoluble, yellow precipitate, which decomposes at a low temperature with evolution of oxygen.

The potassium salt,  $3K_2O_2VO_4 + 2KVO_4 + 2H_2O$ , is obtained by treating a saturated aqueous solution of potassium pervanadate with hydrogen peroxide and potassium hydroxide ( $KVO_4 : 3KOH$ ) until a

yellow solution is formed; it crystallises in yellow, rhombic prisms, is very stable, and remains undecomposed for a long time; 100 grams of water dissolve 0.855 gram of the salt at 19°. It yields oxygen when heated with water, and reacts with concentrated and dilute sulphuric acid in the same manner as the preceding salt. The constituents of the salt are in the ratio  $8K_2O : 5V_2O_5 : 190$  and it contains pyropervanadic acid and pervanadic acid. It is converted into the salt  $(KO)_4V_2O_5 + 3\frac{1}{2}H_2O$  when treated with hydrogen peroxide and potassium hydroxide at 0°; this, which is thrown down as a dirty green, flocculent precipitate on adding alcohol to the solution, quickly decomposes with evolution of oxygen, is easily soluble in water and then decomposes with formation of the salt  $3K_2O_2VO_4 + 2KVO_4 + 2H_2O$  and evolution of oxygen. When the salt  $3K_2O_2VO_4 \cdot 2KVO_4 \cdot 2H_2O$  is treated with hydrogen peroxide and potassium hydroxide at the ordinary temperature, it yields the salt  $V_2O_5(O \cdot OK)_3 \cdot OK + 2H_2O$ , which forms a yellow, flocculent precipitate and is intermediate in composition between the two preceding salts. The constitution of these salts and of related salts of other per-acids is discussed.

E. C. R.

**Preparation of Platinum free from Iridium.** By PAUL BERGSÖE (*Zeit. anorg. Chem.*, 1899, 19, 318—326).—See this vol., i, 320.

**Action of Sulphurous Anhydride on Ruthenium Sulphate.** By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1898, 28, ii, 139—142).—*Ruthenious dithionate*,  $RuS_2O_6$ , is formed when sulphurous anhydride is passed into a solution of ruthenium sulphate,  $Ru(SO_4)_2$ ; it is very soluble in water and is precipitated from its aqueous solution by alcohol as a yellowish-white powder soluble in acids without alteration. On evaporating its aqueous solution at the ordinary temperature over a desiccating substance, ruthenious dithionate is deposited as a pale yellow mass of radiating fibres, composed of optically negative crystals, which are too small to admit of their system being determined. On warming with potassium permanganate solution, it is readily oxidised to sulphate and sulphuric acid, the oxidation being more energetic on boiling, and in this case some perruthenic acid, easily recognisable by its odour, is formed. It is also oxidised by the continued action of chlorine, bromine, nitrohydrochloric acid, hydrochloric acid and potassium chlorate, or nitric acid. The formation of ruthenious dithionate by the action of sulphurous anhydride on the sulphate comprises two distinct phases; the ruthenic sulphate being first reduced to the ruthenious compound, and sulphurous anhydride being subsequently taken up directly by the ruthenious sulphate.

T. H. P.

**Volatilisation of Osmium as Tetroxide in a Current of Air or Oxygen.** By OTTOKAR ŠULC (*Zeit. anorg. Chem.*, 1899, 19, 332—334).—Powdered osmium, when heated in a current of air, becomes oxidised and volatilises below 212°; and in a current of oxygen below 170°, but no volatilisation takes place in a current of oxygen at 155°. The volatilisation in a current of air amounts

to about 0·07 per cent. per hour at 212°, and to about 3 per cent. at 270°; in a current of oxygen, it amounts to about 0·02 per cent. per hour at 170° and to 1·0 per cent. at 215°.

E. C. R.

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## Mineralogical Chemistry.

**Quartz and Opal.** By GIORGIO SPEZIA (*Jahrb. f. Min.*, 1899, i, Ref., 92; from *Atti Accad. Sci. Torino*, 1898, 33, 289—308, 876—882. Compare Abstr., 1897, ii, 406).—The author finds that the solubility of quartz in water does not depend on the pressure, but only on the temperature. By the slow evaporation of the solution, the dissolved silica is deposited in the form of opal, but when alkali is present, it is deposited as quartz. The rhombohedral faces of quartz crystals are the most rapidly attacked, and on the same face there is also a greater deposition of material from a solution of silica obtained by decomposing sodium silicate. The quicker growth of quartz crystals in the direction of the vertical axis explains the common prismatic habit of this mineral.

These directions of maximum and minimum rate of growth of quartz, parallel and perpendicular respectively to the vertical axis, are confirmed by experiments (described in the second paper) on plates of certain thicknesses cut in various directions from quartz crystals.

Opal, when treated in the same manner with water and sodium silicate, is converted into an aggregate of quartz crystals.

L. J. S.

**Associated Minerals of Rhodolite.** By WILLIAM E. HIDDEN and JULIUS H. PRATT (*Amer. J. Sci.*, 1898, [iv], 6, 463—468. Compare Abstr., 1898, ii, 605).—A list has already been given of the minerals identified in the concentrates of the gravels from Mason Branch, Macon Co., North Carolina.

**Quartz:** pseudomorphous, rhombic dodecahedra, probably after garnet. A crystal of sp. gr. = 3.203 was found to consist of a mixture of quartz and rhodolite.

**Gahnite** occurs as rounded octahedral crystals, and as fragments, with a clean, glassy fracture, and a deep bottle-green colour by transmitted light. Sp. gr. = 4.24—4.40. Analysis by C. Baskerville gives the formula  $(12\text{Zn}, 4\text{Fe}, 3\text{Mg})\text{O}, \text{Al}_2\text{O}_3$ . It is, therefore, kreittonite, the zinc-iron variety of gahnite.

$\text{Al}_2\text{O}_3$ .	FeO.	ZnO.	MgO.	Total.
61.09	7.78	27.44.	3.30.	99.61.

**Bronzite** of a pale yellow to deep brown colour is unusual in being perfectly transparent. Sp. gr. = 3.43.

**Cordierite** is abundant in boulders of granular quartz; in the interior, where only slightly altered to mica, it is pure white or yellowish and nearly transparent. Minute flakes of mica enclosed

parallel to the basal plane give a golden sheen. It is wholly devoid of dichroism. An analysis by Baskerville agrees only approximately with the usual formula.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO.	MgO.	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.
47·60	36·20	2·13	10·73	trace	3·14	99·80	2·54

*Staurolite* is of a rich garnet-red and perfectly transparent; sp. gr. = 3·80.

*Gold* in fine scales contains 90·77 per cent. Au; sp. gr. = 17·88.

*Sperryllite* occurs as minute octahedral crystals of pyritohedral symmetry.  
L. J. S.

**Analyses of Tysonite, Bastnäsité, Prosopite, Jeffersonite, Covellite, &c.** By WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1899, [iv], 7, 51—57).—*Tysonite* and *Bastnäsité*.—A crystallised specimen from Cheyenne Mountain, near Pike's Peak, Colorado, consists of tysonite (anal. I) covered on one side with a layer of bastnäsité (anal. II), there being a sharp line of demarcation between the two minerals. Under the microscope, sections show that the tysonite is penetrated by strings and grains of bastnäsité, and that all parts of the former have the same optical orientation. The tysonite contains minute enclosures and negative crystals containing fluid and cuboidal crystals. Besides the bastnäsité, there are other white and brownish alteration products of the tysonite.

	Ce <sub>2</sub> O <sub>3</sub>	La group.	F.	CO <sub>2</sub>	CaO.	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total less O for F.
I.	42·89	39·31	28·71	0·53	0·18	0·11	0·30	—	99·95
II.	37·71	36·29	7·83	20·03	—	0·22	0·18	0·08	99·04

The cerium oxide contains traces of what appears to be thorium. The metals of the lanthanum group have the at. wt. = 139·7 (anal. I) and 141 (anal. II); traces of oxides of the yttrium group may also be present. These analyses establish the formulæ R''F<sub>3</sub> and R''F'CO<sub>3</sub>, which have previously only been assumed for tysonite and bastnäsité respectively.

*Prosopite* of a beautiful green colour occurs in the Dugway mining district, Torvel Co., Utah, associated with fluorite, silver, &c. It is not easy to separate pure material free from quartz grains; H = 4·5; sp. gr. = 2·87. Analysis gave

Al.	Ca.	Mg.	K.	Na.	Cu.	F.	H <sub>2</sub> O.	Quartz and O.	Total.
20·08	17·55	trace	0·12	0·32	0·17	28·00	14·24	19·52	100·00

Neglecting alkalis and copper, and deducting a little calcium fluoride, this gives the prosopite formula, CaAl<sub>2</sub>(F,OH)<sub>8</sub>. Only 1·25 per cent. of water is expelled at 280°.

*Jeffersonite* from Franklin Furnace, New Jersey, is brown, and has a marked lamellar structure in one direction, with other cleavages; sp. gr. = 3·39. Analysis agrees with the usual formula, R'SiO<sub>3</sub>.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO.	ZnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
51·70	0·36	0·37	7·43	3·31	23·68	12·57	0·12	trace	0·65	100·19

Titanium, ferrous oxide, and phosphoric acid are absent. Another

brown substance, from Franklin Furnace, somewhat resembling jeffersonite in appearance, was found on analysis to be a mixture.

*Covellite*, in splendid indigo-blue masses from the East Greyrock mine at Butte, Montana, gave results agreeing closely with the formula  $\text{CuS}$ .

Cu.	S.	Fe.	Insol.	Total.	Sp. gr.
66·06	33·87	0·14	0·11	100·18	4·76

*Enargite* from Butte, gave

Cu.	Fe.	Zn.	As.	Sb.	S.	Insol.	Total.
48·67	0·33	0·10	17·91	1·76	31·44	0·11	100·32

Analyses are also given of mixed hydrated sulphates of copper, aluminium, &c., and of iron, aluminium, &c., from Montana.

L. J. S.

**Rhodochrosite from the Odenwald.** By K. VON KRAATZ-KOSCHLAU (*Jahrb. f. Min.*, 1899, i, Ref. 27; from *Notizbl. Verein f. Erdkunde, Darmstadt*, 1897, [iv], 18, 50—53).—Manganese ores are mined in the Zechstein dolomite near Bockenrod, on the north side of Morsberg. Here pale red, crystalline rhodochrosite encrusts the oxides of manganese, or cements together fragments of dolomite. Distinct crystals are rare; three habits are distinguished:—I, tabular or lenticular, with {111} and  $\{10\bar{1}\}$ ; II,  $\{20\bar{1}\}$  with {111} and  $\{10\bar{1}\}$ ; III,  $\{22\bar{3}\}$  with {111}. Analyses of crystals of each habit gave respectively,

	MnO.	MgO.	CaO.	CO <sub>2</sub> .	Insol.	Total.
I. {	60·89	0·84	1·23	37·00	—	99·96
	60·90	0·33	0·53	36·99	0·55	99·20
II. {	—	1·31	1·14	39·03		
	—	1·12	1·29			
III.	60·87	trace	1·02	38·52	—	100·41

The succession of minerals is: (1) crystallised dolomite, (2) oxides of manganese, (3) barytes, (4) rhodochrosite, (5) barytes. The barytes is pure barium sulphate, and crystals of the two generations differ in habit.

L. J. S.

**Vivianite and Chalybite in Mecklenburg Peat.** By A. GAERTNER (*Jahrb. f. Min.*, 1899, i, Ref. 59; from *Inaug.-Diss. Rostock, Güstrow*, 1897; and *Archiv Ver. d. Fr. d. Naturgesch. Mecklenburg*, 1898, 51, 73—130).—The peat of the Mecklenburg moors contains considerable amounts of iron oxide and phosphoric acid; the maximum amounts, at a depth of 40—60 cm. from the surface, are:  $\text{Fe}_2\text{O}_3$ , 24·75;  $\text{P}_2\text{O}_5$ , 6·75 per cent. (organic matter, 53·41). Layers of colourless compact vivianite contain:  $\text{Fe}_3(\text{PO}_4)_2$ , 32·5—80·0;  $\text{FeCO}_3$ , 14·5—44;  $\text{CaCO}_3$ , 3—34, and in one case, calcium phosphate, 17 per cent. Nodules of chalybite contain:  $\text{FeCO}_3$ , 39—74 per cent., together with variable amounts of ferric phosphate, calcium carbonate, and iron hydroxide. Cavities in the chalybite nodules sometimes contain pale blue, crystallised vivianite.

The iron is considered to have been derived from the numerous

boulders, by the action of humic acid and carbonic anhydride; and the vivianite has been formed by the action of ammonium phosphate, derived from animal remains, on the compounds of iron. L. J. S.

**Formation of Glauber Salt [Mirabilite] in the Kara-bugas Gulf.** By S. KUSNETZOFF (*Zeit. prakt. Geol.*, 1898, 26—27).—In the large shallow Kara-bugas gulf the loss of water consequent on the rapid evaporation is compensated by a flow through the narrow straits from the Caspian Sea. Analysis by Lebedintzeff of Caspian water gave, in 1000 parts,

NaCl.	KCl.	MgCl <sub>2</sub> .	MgSO <sub>4</sub> .	CaSO <sub>4</sub> .	CaCO <sub>3</sub> .
0·780	0·044	0·054	0·304	0·084	0·016

Here  $\text{MgSO}_4:\text{NaCl}=1:2$ , whilst in water of the Black Sea the ratio is 1:11. The conditions are, therefore, favourable for the deposition of sulphates. Near the central portions of the gulf is a deposit, exceeding a foot in thickness and over a considerable area, of transparent crystals of mirabilite ( $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ ), while nearer the shore there are deposits of gypsum on the floor of the gulf.

L. J. S.

**Fibrous Goslarite from Aachen.** By LOUIS GRÄFF (*Jahrb. f. Min.*, 1899, i, 76—77).—In the old workings of the Schmalgraf mine at Altenberg near Aachen, is a fibrous efflorescence with silky lustre, which is the result of the recent decomposition of blende. Analysis gives the usual formula  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ .

ZnO.	FeO.	SO <sub>3</sub> .	H <sub>2</sub> O.	Total.
27·398	0·251	27·978	44·316	99·943

L. J. S.

**Thinolite.** By ARTHUR M. EDWARDS (*Chem. News*, 1898, 78, 294—295).—The author is in possession of specimens from Salt Lake desert in Utah and from Yellowstone Park which he considers to be thinolite.

L. J. S.

**Zoisite from the Alps.** By PIERRE TERMIER (*Bull. Soc. franç. Min.*, 1898, 21, 148—170).—A greenish-white mica-schist from Bobbio in the Cottian Alps contains, besides tremolite and albite, aggregates of small zoisite crystals not exceeding 1 mm. in length. Material of sp. gr. = 3·36 gave analytical results agreeing with the usual zoisite formula,  $\text{HCa}_2(\text{Al}, \text{Fe})_3\text{Si}_3\text{O}_{13}$ , with  $\text{Al}:\text{Fe}=9:1$ .

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
39·45	30·15	4·60	23·29	0·90	0·53	0·31	0·82	100·05

The optic axial plane is approximately parallel to  $c(001)$  and the acute positive bisectrix is nearly normal to  $a(100)$ ;  $\rho > v$ ,  $2V = 35-40^\circ$ ,  $\alpha = \beta = 1·696$ ,  $\gamma = 1·703$ . Zoisite from Vanoise in the Savoy Alps has the same optical characters, and both are distinguished as  $\beta$ -zoisite.

The zoisite first examined by Des Cloizeaux differs optically from the above, and is called  $\alpha$ -zoisite. Here the acute positive bisectrix has the same position as before, but the optic axial plane is approximately parallel to the perfect cleavage  $b(010)$ ; also the dispersion  $\rho < v$  is much greater, and sections parallel to  $a(100)$  do not completely

extinguish, but are coloured violet between crossed nicols in white light. Zoisite from Ducktown in Tennessee, Clay Co. in North Carolina, Sau Alpe, and other localities consists of a regular intergrowth of these two optical varieties, both of which are identical in crystalline form, being probably anorthic with very nearly rectangular axes. L. J. S.

**Composition of Tourmaline.** By SAMUEL L. PENFIELD and H. W. FOOTE (*Amer. J. Sci.*, 1899, [iv], 7, 97—125).—A detailed historical review is given of the several formula which have been proposed for this complex borosilicate by Rammelsberg, Riggs, Wülfing, Scharizer, Jannasch and Kalb, Goldschmidt, Rheineck, Clarke, and Groth. So many analyses have been previously made that it was thought best to make only two accurate ones on very carefully selected material of different types. Anal. I is of clear, colourless, glassy, and perfectly pure tourmaline from De Kalb, St. Lawrence Co., New York; sp. gr.  $>3.033 < 3.065$ . Anal. II is of small, transparent prisms of a uniform pale green colour from Haddam Neck on the Connecticut River; sp. gr. 3.089. After fusing with sodium carbonate, the boron was distilled off with methylic alcohol and weighed as calcium borate (Gooch's method); the presence of fluorine was shown not to affect this reaction. Water and fluorine were determined directly by the methods described by Penfield in 1894. Each of the analyses (I and II) is the mean of two which are in very close agreement.

	SiO <sub>2</sub>	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Li <sub>2</sub> O	H <sub>2</sub> O	F	Total (less O for F)
I.	36.72	0.05	10.81	29.68	0.22	—	14.92	3.49	1.26	0.05	—	2.98	0.93	100.72
II.	36.96	0.03	11.00	30.56	2.14	2.00	0.15	1.28	2.10	—	1.64	3.10	1.13	100.61

These do not give any simple molecular ratios; but by taking the number of hydrogen atoms equivalent to the different metals (for example, Al<sub>2</sub>O<sub>3</sub> replaced by 6H) the ratios become, for I, SiO<sub>2</sub>:B<sub>2</sub>O<sub>3</sub>:H = 4:1:19.90, and, for II, = 4:1.02:19.98. The tourmaline acid is therefore H<sub>20</sub>B<sub>2</sub>Si<sub>4</sub>O<sub>21</sub>. Previous analyses are discussed at length and made to agree with this formula when the necessary corrections are introduced; for example, in Rammelsberg's thirty analyses the determinations of the silica were probably too high, and of the water too low. Tourmalines containing titanium agree better with the present formula when Ti<sub>2</sub>O<sub>3</sub> is assumed rather than TiO<sub>2</sub>.

The ratio SiO<sub>2</sub>:(OH,F) is not constant, but in all analyses the water, when directly determined, is enough for 2(OH) and in only a few cases enough for 3(OH). Further, aluminium is always present in sufficient amount to replace more than half the hydrogen atoms. All varieties of tourmaline may therefore be considered as salts of the aluminium borosilicic acid, H<sub>9</sub>Al<sub>3</sub>(B·OH)<sub>2</sub>Si<sub>4</sub>O<sub>19</sub>. The remaining 9H may be replaced by aluminium, alkalis, magnesium, and iron in varying proportions, and there may also be some basic hydrogen. For example, in the Haddam Neck tourmaline (anal. II), 6.1 H is replaced by Al, 1.1 H by R'', 1.2 H by R', whilst 0.6 is basic hydrogen.

When arranged according to the amount of aluminium present, tourmalines fall into the following groups:—(1) lithia tourmalines,

with much aluminium and little magnesium and iron; these are generally light coloured and transparent, and difficultly fusible, and are found in pegmatite veins: (2) iron tourmalines: (3) magnesia-iron tourmalines; the last two varieties are black or dark brown owing to the presence of iron, and occur in granite, gneiss, and schist, although sometimes also in pegmatite veins: (4) magnesia tourmalines with the least amount of aluminium; these are light coloured and easily fusible, and occur in crystalline contact limestones.

These different varieties are the same in crystalline form, and are isomorphous because of the mass effect of the complex radicle,  $[\text{Al}_3(\text{B}\cdot\text{OH})_2\text{Si}_4\text{O}_{19}]$ , which is so great that alkalis, R" and aluminium must be considered as isomorphous constituents, just as sodium ( $\text{Na}_2$ ) and calcium are isomorphous in the complex zeolites and in the sodalite-garnet group, although they are not isomorphous in more simple compounds.

*Detection of Ferrous and Ferric Iron in Silicates.*—The determination of ferrous iron by the ordinary method of decomposing the mineral with hydrofluoric and sulphuric acids is scarcely applicable in the case of tourmaline, as this mineral is extremely insoluble in these acids. It may be fused with borax in an inert atmosphere, decomposed with sulphuric acid, and titrated with potassium permanganate; by this method, however, a certain small proportion of the ferric iron is reduced; but the method is of easy application for the qualitative testing for ferrous and ferric iron in silicates. L. J. S.

**Secondary Minerals in Andesite from Santorin.** By ALFRED LACROIX (*Compt. rend.*, 1897, 125, 1189—1191).—Cavities in hornblende-andesite from the Island of Thera, Santorin, Grecian Archipelago, are lined with crystals of tridymite, fayalite, biotite, magnetite, and hornblende. These minerals have been formed—the tridymite from the glassy base, and the others from the ferromagnesian minerals—by the action of water vapour liberated during the consolidation of the lava. Evidence of similar secondary action is seen in a tuff, the lapilli of which are coated with delicate needles of hypersthene. L. J. S.

**Rocks and Minerals from Oaxaca, Mexico.** By HANS LENK (*Jahrb. f. Min.*, 1899, i, Ref. 73—84; from *Beiträge zur Geol. u. Palæont. d. Republik Mexico*, 1898, 2, 57—142).—In a petrographical paper, the following analyses are given of minerals isolated from the rocks of the State Oaxaca in Mexico. The rocks of this district are mainly Archæan penetrated by old eruptives; to the north are crystalline schists underlying sedimentaries of Cretaceous age, these being partly covered by recent volcanic rocks. *Garnet.* Analysis I, yellowish to brownish-red isotropic crystals of almandine in garnet-gneiss from Sierra de Cimaltepec. II, rose-coloured in garnet-granulite from Las Sedas between Huitzo and Nochixtlan. *Diopside.* III, pale greyish-green and transparent in pyroxene-gneiss from Sierra Ejutla. IV, pale green in graphite-granulite between Pochutla and Puerto Angel; formula,  $2\text{MgAl}_2\text{SiO}_6 + 16\text{CaFeSi}_2\text{O}_6 + 29\text{CaMgSi}_2\text{O}_6$ . V, greyish-green, of diallage habit, in an augite-scapolite rock north of Rancho

Zopilote, Serrania de Ejutla; formula,  $4\text{MgAl}_2\text{SiO}_6 + 8\text{CaFeSi}_2\text{O}_6 + 38\text{MgCaSi}_2\text{O}_6$ . VI, pale green and transparent, with  $c : t = 39^\circ 12'$ ,  $\beta_{\text{Na}} = 1.6820$ ,  $2V = 58^\circ 48'$ , in a granular limestone, rich in augite and scapolite, from north of Rancho Zopilote; formula,  $\text{MgFe}_2\text{SiO}_6 + 3\text{MgAl}_2\text{SiO}_6 + 22\text{CaFeSi}_2\text{O}_6 + 78\text{CaMgSi}_2\text{O}_6$ .

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
I.	36.43	25.97	—	28.12	3.14	3.58	1.88	99.12	4.173
II.	39.24	21.89	—	24.37	0.82	7.29	6.73	100.34	3.98
III.	53.38	2.13	—	4.75	—	24.69	?	—	3.214
IV. [52.22]	1.91	—	—	10.76	—	23.53	11.58	100.00	—
V.	51.89	4.18	—	4.87	—	23.38	15.31	99.63	3.108
VI.	52.46	1.31	0.68	6.78	—	23.98	14.04	99.25	3.197

*Scapolite*. VII, granular, probably derived from plagioclase; from the same rock as V; formula,  $7\text{Me}5\text{Ma}$ . VIII, long prisms from the same rock as VI;  $\omega = 1.569$ ,  $\epsilon = 1.550(\text{Na})$ ; formula,  $5\text{Me}3\text{Ma}$ .

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Cl.	SO <sub>3</sub>	H <sub>2</sub> O.	Total.	Sp. gr.
VII.	49.37	27.46	trace.	13.98	0.21	1.08	5.57	1.19	0.02	1.96	100.84	2.697
VIII.	49.09	27.95	trace.	15.71	trace.	0.33	5.02	1.50	—	1.17	100.77	2.738

*Heulandite*. IX, platy masses and small crystals lining crevices in amphibole-andesite from Cerro Yolomecatl. Goniometric measurements are given.  $\text{Si} : \text{Al}_2 : \text{Ca} : \text{H}_2\text{O} = 5.89 : 1 : 0.77 : 5.46 : 21.03$ . At  $125^\circ$ , there is a loss of 4.05 per cent. of water, at  $175$ — $200^\circ$ , 8.51, and at  $250$ — $260^\circ$ , of 9.37 per cent.

*Sphene*. X, crystals in a zoisite-augite rock from Sierra Ejutla. Optical determinations are given.

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	FeO.	CaO.	SrO.	H <sub>2</sub> O.	Total.	Sp. gr.
IX.	59.32	—	17.12	—	—	7.25	trace.	16.48	100.17	2.182
X.	28.84	41.35	2.98	trace.	1.33	25.27	—	—	99.77	3.51

Several other partial analyses of minerals and several rock analyses are given.

L. J. S.

**Formation of Dolomite in the Alps.** By E. PHILIPPI (*Jahrb. f. Min.*, 1899, i, 32—46).—A review is given of the various theories which have been proposed to account for the formation of dolomite, and the following is put forward. Most limestones contain a small amount of magnesium carbonate; further, calcium carbonate is more readily soluble in water than magnesium carbonate, so that the leaching out of calcium carbonate by sea water, or by percolating rain water, would increase the relative amount of magnesium carbonate in the residue. A case supporting this theory is described from the Passo di Pallio, near Lecco, in Lombardy; a highly crystalline and friable light yellowish dolomite can here be seen to be the weathered product of a compact dark-brown dolomitic limestone. Analyses of material taken from different parts of the same hand-specimen gave: I, for the inner portion of dark compact limestone (containing, as shown by the analysis, 5.56 per cent. of dolomite); II, for the intermediate zone (87.02 per cent. of dolomite); III, the outer light-coloured crystalline portion; IV, the sand rubbed from the surface—the last two consisting of almost pure dolomite ( $\text{MgCO}_3, \text{CaCO}_3$ ).

	CaO.	MgO.	Insoluble.
I.	54.15	1.38	0.81
II.	35.86	17.38	0.16
III.	31.38	21.04	0.28
IV.	31.33	20.90	0.16

Under the microscope, the specimens I and II show rhombohedra of dolomite set in a finely crystalline ground-mass of calcite.

L. J. S.

**Meteoric Irons.** By EMIL W. COHEN (*Ann. k.k. naturhist. Hofmus. Wien*, 1899, 13, 118—158).—A summary of the literature and a detailed description of the structure of the following irons is given.

I, *Campo del Cielo*, Gran Chaco Gualamba, Argentina. This is a granular to compact ataxite composed of nickel-iron having the composition of kamacite. The etched surface appears, to the unaided eye, finely granular and homogeneous, but with a lens it shows characteristic ridges and hollows, and by deeper etching, wrinkled etch-faces. Wöhler's iron, and others, which have sometimes been considered to belong to Campo del Cielo, are quite distinct.

II, *Siratik*, Senegal, West Africa. This iron in structure and composition closely resembles the Campo del Cielo iron. It is possible that different specimens under this name may belong to different falls.

III, *Santa Rosa*, Colombia, South America. This is the mass of iron, weighing about 750 kilos., in the market-place at Santa Rosa. It is an octahedral iron of coarse structure (Zacatecas group).

IV, *Tocavita*, near Santa Rosa. Certain fragments, labelled as Santa Rosa, are found to belong to a different type; these it is proposed to distinguish as "*Tocavita*," after the name of the hill where they were found. The structure is octahedral, with very fine lamellæ, closely resembling that of the Ballinoo iron (*Abstr.*, 1898, ii, 440). It is further distinguished by the presence of much rhabdite, sometimes in large crystals. A second determination of the phosphorus gave 0.52 per cent., corresponding with 3.38 per cent. of rhabdite.

V, *Rasgata*, Colombia (compare *Abstr.*, 1897, ii, 57). This is an ataxite, and closely resembles Santa Rosa in composition.

VI, *Linnville Mountain*, Burke Co., North Carolina. This is an ataxite rich in nickel.

VII, *Chesterville*, Chester Co., South Carolina (compare *Abstr.*, 1898, ii, 83). A granular to compact ataxite poor in nickel.

VIII, *Kokomo*, Howard Co., Indiana. In the granular structure and in the composition, this resembles the Cape of Good Hope iron.

IX, *Iquique*, Tarapaca, Peru. In structure and composition, this resembles the last.

X, *Long Creek*, Jefferson Co., Tennessee. The structure and composition of this is that of cast iron; it is, therefore, a pseudo-meteorite. Analysis X, also Mn, 0.16; SiO<sub>2</sub>, 1.39 per cent. Analyses by O. Sjöström of these irons gave I—X respectively.



	Fe.	Ni.	Co.	Cu.	Cr.	C.	P.	S.	Cl.	Total.
I.	94.25	5.11	0.57	0.03	0.03	0.06	0.18	0.05	trace	100.28
II.	94.07	5.21	0.77	0.01	—	0.01	0.26	0.04	—	100.37
III.	92.30	6.52	0.78	0.02	trace	0.18	0.36	0.04	nil.	100.20
IV.	89.81	9.77	0.57	0.02	trace	0.03	0.22	0.06	nil.	100.48
V.	92.81	6.70	0.64	0.01	trace	0.19	0.28	0.08	trace	100.71
VI.	83.13	16.32	0.76	0.02	—	0.11	0.23	0.02	—	100.59
VII.	93.80	5.50	0.75	0.02	trace	0.02	0.34	0.03	nil.	100.46
VIII.	83.24	15.76	1.07	0.01	—	—	0.08	trace	—	100.16
IX.	83.49	15.41	0.94	0.02	trace	0.03	0.07	0.02	—	99.98
X.	94.20	nil.	nil.	—	—	4.37	0.11	—	—	100.23

These analyses correspond with the following mineralogical composition.

			Ni-Fe Nickel-iron. phosphide.	FeS.	Sp. gr.	
I.	Campo del Cielo	...	98.69	1.17	0.14	7.7679
II.	Siratik	...	98.21	1.68	0.11	7.7752
III.	Santa Rosa...	...	97.55	2.34	0.11	7.6896
IV.	Tocavita	...	98.42	1.42	0.16	7.8504
V.	Rasgata	...	97.97	1.81	0.22	7.6540
VI.	Linnville Mtn.	...	98.46	1.49	0.05	7.4727
VII.	Chester ville	...	97.72	2.20	0.08	7.8209
VIII.	Kokomo	...	99.48	0.52	—	7.8606
IX.	Iquique	...	99.50	0.45	0.05	7.8334

L. J. S.

**Platinum and Iridium in Meteoric Iron.** By JOHN M. DAVISON (*Amer. J. Sci.*, 1899, [iv], 7, 4).—The residue remaining after dissolving 608.6 grams of the Coahuila (Mexico) iron in hydrochloric acid contained 0.014 gram of metallic platinum and 0.0015 gram of a black powder insoluble in aqua regia; the latter, after fusion with zinc, was dissolved, and with ammonium chloride yielded a dark-red, crystalline precipitate, probably of ammonium iridichloride. From 464 grams of the Toluca (Mexico) iron, a few crystals of potassium platinochloride were prepared; these were reddish in colour, no doubt due to the presence of iridium. L. J. S.

**Mineral Water from Radein, Styria.** By ANTON FRANZ REIBENSCHUH (*Mitth. Ver. Steiermark*, 1898, 34, 177—186).—Water from the "Neubrunnen" at Radein is perfectly clear, and has an acid taste; temperature 13.2° (that of the air being 21°); sp. gr. = 1.0061 at 21°. In 10,000 parts by weight it contains: K<sub>2</sub>SO<sub>4</sub>, 3.75637; Na<sub>2</sub>SO<sub>4</sub>, 1.04715; NaCl, 7.17978; Na<sub>2</sub>CO<sub>3</sub>, 35.32533; Li<sub>2</sub>CO<sub>3</sub>, 0.16172; CaCO<sub>3</sub>, 4.13183; MgCO<sub>3</sub>, 2.50100; FeCO<sub>3</sub>, 0.16028; Al<sub>2</sub>O<sub>3</sub>, 0.10191; SiO<sub>2</sub>, 0.18971; total solids, 54.55508; CO<sub>2</sub> in bicarbonates, 17.93510; CO<sub>2</sub> free, 23.90963; total, 96.39981. Also traces of phosphoric acid and strontium. This composition is very similar to that of the principal spring at Radein (*Abstr.*, 1896, ii, 435). L. J. S.

**Fluorine in the Waters of Nérís-les-Bains.** By P. CARLES (*J. Pharm.*, 1898, [vi], 8, 566—567).—The effect of these waters in

making glass dull is due to the deposition of salts, chiefly calcium carbonate, and not to the action of fluorine. The fluorine is present in the waters as calcium fluoride, and not as sodium fluoride.

H. R. LE S.

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## Physiological Chemistry.

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**Temperature of the Mouth after Exercise.** By MARCUS S. PEMBERTY (*Proc. Physiol. Soc.*, 1899, 21).—The mouth temperature is untrustworthy, and is not a real measure of the internal heat of the body, especially after the cooling of the mouth which is produced by exercise, or in cold weather. Buccal respiration, moreover, in man plays a part in the regulation of the temperature during exercise.

W. D. H.

**Temperature of the Horse.** By GERMAN SIMS WOODHEAD (*Proc. Physiol. Soc.*, 1899, 15—18).—The figures given are numerous, and show that the temperature of the horse during rest is lower than that previously stated, and the rise of temperature on muscular exertion is more marked also.

W. D. H.

**Absorption of Proteids.** By P. A. LEVENE and I. LEVIN (*Proc. Amer. Physiol. Soc.*, 1898, 17. *Amer. J. Physiol.* 2).—The difficulty of studying proteid absorption is that after the intestinal wall has been passed, it is not possible to distinguish between the proteids absorbed and those already in the tissues and fluids of the body. To obviate this, iodo-proteid was used; this was placed in a loop of intestine, and then looked for in the thoracic duct; it was not found there. The result confirms the old theory, that proteids are absorbed by the blood vessels, not by the lymph, as Asher and Barbéra consider.

W. D. H.

**Absorption from the Peritoneal Cavity.** By LAFAYETTE B. MENDEL (*Proc. Amer. Physiol. Soc.*, 1898, 16. *Amer. J. Physiol.*, 2).—Certain coloured substances, like indigo-carmin, after they have been injected into the peritoneum, appear in the urine earlier than in the thoracic duct. This confirms Starling's statement that absorption is carried out by the blood vessels.

W. D. H.

**Peptic and Tryptic Digestion of Proteid.** By D. LAWROFF (*Zeit. physiol. Chem.*, 1899, 26, 513—523).—After weak gastric digestion of fibrin, products are obtained which are not precipitable by ammonium sulphate, and which do not give some of the characteristic reactions of proteids. If digestion is energetic and prolonged, the products which are precipitated by ammonium sulphate, and those which are not so precipitable, fail to give the proteid reactions; even the biuret reaction in some cases is negative. The substances are crystallisable and are precipitable by alkaloidal reagents. Corresponding results are obtained on tryptic digestion. Rennin has no action on

the products of peptic and tryptic digestion. Experiments with dry heat show that at 100° Danilewsky's peptone is dehydrated.

W. D. H.

**Inulin in the Gastro-intestinal Tract.** By RUSSELL H. CHITTENDEN and ARTHUR B. SIVITER (*Proc. Amer. Physiol. Soc.*, 1898, 18—19. *Amer. J. Physiol.*, 2).—Ptyalin, amyllopsin, diastase, and taka-diastase have no action on inulin. Dilute hydrochloric acid (0.05 to 0.2 per cent.) inverts it into levulose, and hydrochloric acid combined with proteids acts in the same way, but more slowly. This inversion probably occurs in the stomach; oxalic, lactic, and salicylic acids act similarly.

W. D. H.

**Choline and Neurine in the Intestine during its complete Obstruction.** By BEATTIE NESBITT (*Proc. Amer. Physiol. Soc.*, 1898, 8; *Amer. J. Physiol.*, 2).—Yolk of egg was given to dogs, and the intestines closed; two or three days later, when the animals were killed, choline, neurine, and a ptomaine of uncertain composition were separated from the intestinal contents. The origin of the choline and neurine was doubtless the lecithin of the food.

W. D. H.

**Influence of the Kidney on Metabolism.** By JOHN ROSE BRADFORD (*J. Physiol.*, 1899, 23, 415—496).—Excision of a part of one kidney in dogs is followed by some atrophy of that organ and a slight transitory wasting of the body. Approximately, two-thirds of the total kidney weight can be removed without a fatal result; there is a considerable and permanent increase of the urinary water. If three-quarters of the kidney weight be removed, death occurs in from one to six weeks; there is great wasting and weakness, but no coma or convulsions; the amount of urinary water and urea excreted is much increased. There is considerable increase also in the nitrogenous extractives in blood and tissues, particularly in the muscles. Excision of large quantities of liver substance does not give rise to the same disturbances. The experiments do not show whether or not the increase of katabolism is due to the cessation of an internal secretion normally supplied by the kidney.

W. D. H.

**Metabolism in Fishes.** By KARL KNAUTHE (*Pflüger's Archiv*, 1898, 73, 490—500).—The experiments made on carp show the great share the proteids take in the total metabolic exchanges, the important influence of temperature on the metabolism of proteid, and in the nutrition of the animals the importance of mineral substances for the purposes of assimilation and digestion.

W. D. H.

**Action of Suprarenal Extract on the Mammalian Heart.** By GEORGE B. WALLACE and W. A. MOGK (*Proc. Amer. Physiol. Soc.*, 1898, 5. *Amer. J. Physiol.*, 2).—Suprarenal extract stimulates the vagus centre and directly stimulates the heart muscle as well as the muscular tissue of the arterioles.

W. D. H.

**Action of Animal Extracts, Bacterial Cultures, and Culture Filtrates on Mammalian Heart-muscle.** By ALLEN CLEGHORN (*Amer. J. Physiol.*, 1899, 2, 273—290).—The various substances

investigated were added to blood perfused through portions of the excised dog's heart. Suprarenal extract was the most powerful; it causes marked augmentation of the extent and rate of the contractions of the apex; after a time, fibrillary contractions occurred. Extract of the pituitary body, lessens the rate but increases the amplitude; extract of the infundibulum is more powerful and lessens both the rate and amplitude of the beats. Orchitic extract in small doses increases the force of the heart; larger doses decrease the tonus and increase the rhythm. Extracts of liver, pancreas, submaxillary gland, and spleen are almost inactive. Extract of kidney causes a slight fall in tonus and rate; extract of thyroid temporarily augments the force and rate, except when large doses are used; then the effect is reversed. Cultures of various bacteria affect the apex in a mechanical way; the filtrates are purely depressant, although by no means markedly so.

W. D. H.

**Cholesterol of the Blood.** By EBERHARD HEPNER (*Pflüger's Archiv*, 1898, 73, 595—606).—The blood corpuscles contain cholesterol in the free condition, compounds of cholesterol with fatty acids being absent; in the corpuscles of the horse, the average percentage of cholesterol is 0.275, and in the dog, 0.552. During hunger, the quantity sinks. The blood plasma under certain circumstances (not yet clearly defined) may contain free cholesterol in addition to salts of that substance.

W. D. H.

**Cholesterylic Salts of Bird's Blood.** By ERNEST W. BROWN (*Amer. J. Physiol.*, 1899, 2, 306—309).—Cholesterylic oleate and palmitate were separated from the blood serum of numerous birds. Free cholesterol occurs in the corpuscles.

W. D. H.

**Electrical Conductivity of Animal Fluids.** By WILHELM RÓTH (*Virchow's Archiv*, 1898, 154, 466—500).—The determination of the molecular concentration of the blood-serum of ox, sheep, and pig gave a constant result; the depression of the freezing point lies between  $0.55^{\circ}$  and  $0.60^{\circ}$ . The electrical conductivity is fairly constant (96.4 to 104.6 [ $\times 10^{-8}$ ] mercury units); this corresponds with a 0.66 to 0.71 per cent. solution of sodium chloride. Among the electrolytic molecules, sodium chloride forms a nearly constant fraction. From this is deduced a theory of the regulation of the osmotic pressures of the body-fluids. The conductivity of the whole blood is less than that of the serum, and shows considerable variations; this is due to the corpuscles.

A number of observations are also recorded on human urines, normal and pathological; the molecular concentration varies within wide limits ( $\Delta = 0.8$  to 1.94 per cent.); urea does not diminish the conductivity nearly so much as proteid. In normal urine, the ratio of the total molecular concentration and the concentration of the molecules containing chlorine is nearly constant,  $\Delta/\text{NaCl}$  per cent. = 1.14 to 1.79, but in pathological urine this is not the case,  $\Delta/\text{NaCl}$  per cent. = 1.77 to 7.1.

W. D. H.

**Solution of Mercury in the Body Juices.** By A. S. CHITTENDEN (*Proc. Amer. physiol. Soc.*, 1898, 6; *Amer. J. Physiol.*, 2).—By intro-

ducing finely divided mercury into the circulation, mercury is obtained in the urine, but not in the fæces. The body juices can, therefore, dissolve metallic mercury.

W. D. H.

**Muscle Fatigue.** By FREDERIC S. LEE (*Proc. Amer. Physiol. Soc.*, 1898, 11; *Amer. J. Physiol.*, 2).—The fatigue process was studied in the frog, turtle, and cat. The contraction phase is greatly lengthened in the turtle, slightly in the frog, but not at all in the cat. The relaxation is greatly lengthened in the frog and turtle, but only slightly in the cat. Diminution in lifting power is the essential factor in all cases. The sole cause of fatigue is the accumulation of fatigue-products, not decrease of contractile substance. Fatigue, in fact, is a safeguard against exhaustion.

W. D. H.

**Chemistry of Reticular Tissue.** By M. CHRISTINE TEBB (*Proc. Physiol. Soc.*, 1899, 10—11).—The fibres of reticular tissue are anatomically continuous, and identical with the white fibres of connective tissue; Siegfried states, however, that they are different, for they yield not only gelatin, but also a new substance, reticulin. In the present investigation, reticulin was searched for both in the ordinary white fibres of tendon, and in the reticular fibres of the intestinal mucous membrane, but with negative results. Full details are promised later.

W. D. H.

**Conversion of the Liver Glycogen into Glucose.** By DIARMID NOËL PATON (*J. physiol.*, 1899, 24, 36—41).—The statements of previous workers that a diastatic enzyme may be prepared from the blood and tissues by means of alcohol is confirmed. The observations do not indicate that it is present in greater abundance in the liver than in other parts. The amylolytic action of the liver is frequently more powerful after treatment with alcohol. Chloroform, which accelerates the rate of amylolysis in the *post mortem* liver, does not influence, and may even retard, the amylolytic action of the alcohol liver. The opinion that hepatic amylolysis is not due to an enzyme is still adhered to.

W. D. H.

**Maximum Production of Hippuric Acid in Rabbits.** By F. H. PARKER and GRAHAM LUSK (*Proc. Amer. Physiol. Soc.*, 1898, 14. *Amer. J. Physiol.*, 2).—If a quantity of benzoic acid (as lithium salt) is given to fasting rabbits in quantity sufficient to unite with the glycocine formed in the animal, but not sufficient to produce toxic symptoms, a fixed ratio will exist between the hippuric acid nitrogen and the total nitrogen of the urine. This ratio (1:20) indicates that 5 per cent. of the proteid nitrogen may be eliminated as glycocine. The ratio is not increased by feeding with carbohydrates or gelatin.

W. D. H.

**Iodine in the Tissues after the Administration of Potassium Iodide.** By P. A. LEVENE (*Proc. Amer. Physiol. Soc.*, 1898, 15. *Amer. J. Physiol.*, 2).—The experiments recorded show that only certain keratins, such as that of the hair, only certain proteids, such as those of the thyroid, and only certain fats are capable of uniting with iodine in the organism.

W. D. H.

**Protamine of Mackerel Spermatozoa.** By D. KURAÉEFF (*Zeit. physiol. Chem.*, 1899, 26, 524—534).—The sulphate of the protamine (*scombrine*) separated from the spermatozoa of the mackerel, has the formula  $C_{30}H_{60}N_{16}O_6 \cdot 2H_2SO_4$ , but the chromate has the formula  $C_{30}H_{58}N_{16}O_{5.5} \cdot 2H_2CrO_4$ , that is, contains  $H_2$  and O less than the sulphate. There are other differences (in solubility, optical activity) between the new protamine and others previously described. By decomposing it with sulphuric acid, less nitrogen is eliminated as arginine and histidine than is the case with clupeine and sturine.

W. D. H.

**Pigments of *Aplysia punctata*.** By CHARLES A. MACMUNN (*J. Physiol.*, 1899, 24, 1—10).—*Aplysiopurpurin* is a purple pigment secreted by the dermal glands of various species of *Aplysia*; it is extremely unstable, and rapidly changes into other pigments, even when kept in distilled water or in alcohol protected from the light and air. Although there is no reason to suppose that the material is a mixture of pigments, it differs somewhat in different species. It may be obtained in an approximately pure condition by a method which is described fully, but of which the chief feature is precipitation with ammonium sulphate. The integument contains whitish deposits, in which guanine was detected in small quantity. Spectroscopic plates accompany the paper.

W. D. H.

**Chemical Composition of the Shells of *Crania*, *Terebratulina*, and *Waldheimia*.** By FRANZ KUNCKELL (*J. pr. Chem.*, 1899, [ii], 59, 101—104).—These shells consist mainly of calcium carbonate; those of *Crania* contain more organic matter and more magnesium. They are also sharply distinguished from the shells of *Rhynchonella* and *Lingula*, which consist mainly of calcium phosphate, those of *Lingula* being further distinguished by the presence of a very large quantity of organic matter.

	<i>Crania anomala</i> , O.F.M.	<i>Terebratulina caput serpentis</i> , L.	<i>Waldheimia oranium</i> , O.F.M.
CaCO <sub>3</sub> .....	87.8	94.6	96.2
CaSO <sub>4</sub> .....	2.15	2.4	0.9
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	0.28	—	0.18
CaO .....	—	—	0.3
MgCO <sub>3</sub> .....	3.4	1.05	—
MgO .....	1.8	—	0.6
Organic matter ..	4.3	2.55	2.00
	99.73	100.60	100.18

C. F. B.

**Elimination of Water and of Carbonic Anhydride by the Skin.** By WAKELIN BARRATT (*J. Physiol.*, 1899, 24, 11—18).—When the skin is normal, the elimination of water is reduced to 78 per cent. of the normal output; in dry inflammation, the reduction is 56 per cent. In both cases, the diminution is due to mechanical blocking of the sweat ducts. Water is, however, capable of passing through the keratin-holding epidermis. The elimination of carbonic anhydride is due to a single process, namely, that of diffusion.

W. D. H.

**Relation between Total Nitrogen of Urine and the Nitrogen present as Urea.** By HENRI MOREIGNE (*J. Pharm.*, 1898, [vi], 8, 345—350, 400—405. Compare Abstr., 1899, ii, 73).—The ratio of urea nitrogen to total nitrogen in the urine of six normal subjects fed on a mixed diet varies from 86·2 (minimum) to 88·9 (maximum), with a mean of 87·5; a diet rich in meat raises this ratio from 87·7 to 90·2, an increase of 2·5 per cent. The author reviews the several causes (pathological, &c.) which may modify this ratio, and draws attention to the fact that if chloroform is added to the urine as a preservative, serious errors may arise in the determination of the urea by the hypobromite method, since chloroform vapour is evolved with the nitrogen. In estimating the nitrogen present as urea, it is not advisable to use basic lead acetate, as the nitrogenous substances are not completely precipitated by it. In subsequent experiments, in which the author employed the modified method of Mörner and Sjöquist, and the phosphotungstic acid method (this vol., ii, 72—73), he obtained for the ratio of urea nitrogen to total nitrogen a value of from 76 to 79. A formula is given for calculating the error due to the nitrogen retained by the hypobromite solution.

H. R. LE S.

**Excretion of Urea and of Uric Acid.** By WILLIAM BAIN and WILFRID EDGECOMBE (*J. Physiol.*, 1899, 23, 499—511).—The experiments made on the authors' persons lasted 77 days, the diet was carefully noted throughout and was constant, and the result of the addition of the following liquids was investigated. The saline-sulphuretted Harrogate water acted as a purgative, caused a fall in the 'worth of the blood corpuscles,' lessened the uric acid, and increased the amount of urea eliminated. Chalybeate waters caused a rise in the 'worth of the corpuscle,' or left it unaffected, and lessened the excretion of uric acid; the return to normal was more rapid than with the sulphuretted water. Tea and coffee lessened the uric acid. There is an inverse ratio between the daily excretion of uric acid, and the daily number of leucocytes.

W. D. H.

**Excretion of Bases in the Urine of Fasting Rabbits.** By K. KATSUYAMA (*Zeit. physiol. Chem.*, 1899, 26, 543—557).—During inanition, rabbits lose in the urine much more potassium than sodium. The calcium sinks for some days, and then slowly increases until death; but the magnesium steadily sinks.

W. D. H.

**Extraction of Homogentisic Acid (Quinolacetic Acid) from Urine.** By ARCHIBALD E. GARROD (*J. Physiol.*, 1899, 23, 512—514).—In two cases of alcaptonuria, the following simple method of extracting homogentisic acid was adopted. The urine is heated nearly to boiling, and 5—6 grams of normal lead acetate added per 100 c.c. of urine; the precipitate is filtered off, and the filtrate put in a cool place. At the end of 24 hours, there is complete precipitation of lead homogentisate in a crystalline form, and the acid may be obtained from this by the use of hydrogen sulphide.

W. D. H.

**Cryoscopic Examination of Urine.** By CH. BOUCHARD (*Compt. rend.*, 1899, 128, 64—67).—When nutrition is perfect, the large and com-



plex molecule of albumin is broken down into simple and comparatively small molecules such as urea ; when nutrition is imperfect, substances such as creatinine, uric acid, and a ptomaine, with molecular weights intermediate between those of urea and albumin, are formed, and are eliminated in the urine. It follows that the mean molecular weight of the substances dissolved in the urine will afford indications as to the character of nutrition.

Normal undiluted urine freezes at about  $-1.35^{\circ}$ , but the freezing point may vary between  $-0.50^{\circ}$  and  $-2.24^{\circ}$  in different pathological conditions. In order to determine the mean molecular weight of the dissolved substances, the total quantity of solid matter is estimated, the sodium chloride is estimated separately, and the freezing point is ascertained after diluting the urine with from 1 to 5 times its own volume of water to prevent separation of any dissolved matter. The quantity of sodium chloride present is subtracted from the total solids, and the reduction of freezing point attributable to the sodium chloride is subtracted from the observed reduction. The mean molecular weight  $P$  of the dissolved substances other than sodium chloride is then given by the formula  $P \times 18.5/C$ , where  $C$  is the reduction of freezing point not due to sodium chloride.

In normal human urine, the mean molecular weight is 62 or 63, and very rarely reaches 68 ; it is also very rarely below 60. In illness, however, it varies from 68 to 112, except in some cases of high fever when it tends towards the normal value. It is always high in cases of tuberculosis, and high, and sometimes very high, in cases of chronic nephritis. Sometimes the high value indicates the occurrence of diseases, such as syphilis, or of sequelæ which otherwise would escape recognition.

C. H. B.

**Physiological Action of Choline and Neurine.** By FREDERICK W. MOTT and WILLIAM D. HALLIBURTON (*Proc. physiol. Soc.*, 1899, 9—10).—It has been previously shown (*Abstr.*, 1897, ii, 222 ; 1898, ii, 242) that cerebro-spinal fluid from cases of general paralysis of the insane contains choline, and that the fall of arterial blood pressure that takes place when the fluid is injected into animals is due to this substance. This base is absent from normal cerebro-spinal fluid, and is doubtless in the pathological fluid derived from the disintegration of lecithin in the cerebral tissue. The proof that the base is choline rests partly on its chemical identification in the fluid, and partly on the identical action which the fluid has with weak solutions (0.2 per cent.) of choline or choline hydrochloride. The closely related, and much more toxic, base neurine is absent.

In the case of choline, the fall of blood pressure is produced by vascular dilatation, especially in the intestinal area. Contrary to expectation, the spleen does not participate in this dilatation, but is constricted ; this constriction is followed by an increase of the normal splenic waves. It seems probable that the material in extracts of brain which Schäfer and Moore (*J. Physiol.*, 20, 26) found to produce the same effect is choline. Neurine produces a much more intense constriction of the spleen, but no exaggeration of the splenic waves follows. The action of the base on the intestinal blood vessels is due

to its action on the neuro-muscular mechanism of the blood vessels themselves. This was demonstrated by locally bathing the mesenteric vessels with solutions of choline; and by the fact that choline still continues to produce the usual fall of arterial pressure: (1) after the spinal cord has been divided high up; (2) after the splanchnic nerves have been cut; and (3) after the animal has been poisoned with nicotine; the last method excludes any action of peripheral ganglia.

Neurine produces a fall of blood pressure (chiefly due to its action on the heart); this is followed by a rise of pressure due to constriction of peripheral vessels. Using the same methods as in the investigation of choline, this is not an action on the central nervous system. The constriction of the vessels is, however, probably due to the action of the base on the peripheral ganglia, for after nicotine poisoning it does not occur.

The animals used have been dogs, cats, and rabbits. These were always anaesthetised with ether, chloroform, or A.C.E. mixture; in some cases, they also had a subcutaneous injection of morphine. If, however, a small amount of atropine is mixed with the morphine, the effect of choline is always a rise of blood pressure; the lever of the intestinal oncometer also rises. This fact is not without importance as showing how one poison may modify the action of another, and its bearing on general paralysis will be pointed out in the full paper which will be published shortly.

W. D. H.

**Physiological Action of Eucaine-B. and Analogous Substances.** By GAETANO VINCI (*Virchow's Archiv*, 1898, 154, 549—559. Compare Abstr., 1898, ii, 86).—The action of eucaine-B. was compared with that of triacetoneamine, triacetonealkamine, and triacetonealkaminecarboxylic acid. The carboxyl group appears to have a highly stimulating action, and a curare-like effect on nerve endings. The introduction of an alkyl radicle into the molecule of eucaine and allied substances alters their action and increases their toxicity.

W. D. H.

**Pathological Effects due to Increase of Oxygen Tension.** By JAMES LORRAIN SMITH (*J. Physiol.*, 1899, 24, 19—35).—Oxygen at the tension of the atmosphere stimulates the lung cells to active absorption; at a higher tension, it acts as an irritant and produces inflammation. This conclusion, based on experiments on mice, has a direct bearing on caisson disease. The workers in caissons are occasionally under an air pressure of 4.25 atmospheres, and are undoubtedly within a very short distance of an atmosphere dangerous from the oxygen tension alone.

W. D. H.

**Excretion of Phosphorus and of Nitrogen in Leucæmia.** By W. HALE WHITE and F. GOWLAND HOPKINS (*J. Physiol.*, 1899, 24, 42—47).—Particulars of two cases of leucæmia are given. The main result is that the observations definitely negative the existence of any proportionality between the number of leucocytes and the excretion of those products (phosphoric acid and alloxuric substances) which result from the breaking down of nucleins. Much has still to be learnt concerning the general metabolism in this disease. Milroy and

Malcolm arrived at much the same conclusion ; they, however, do not appear to have noted the diet of their patient. W. D. H.

**Presence of Tyrosine and Leucine in Urine from a case of Cystinuria.** Detection of Tyrosine. By HENRI MOREIGNE *J. Pharm.*, 1898, [vi], 8, 484—487).—The author has isolated both leucine and tyrosine from a specimen of cystinuria urine. The tyrosine was detected by the following method, which is also applicable to other urinary sediments, calculi, &c. A small portion of the urinary sediment is placed on a microscope slide and moistened with a drop of concentrated hydrochloric acid ; this dissolves the cystine and other substances, but leaves the tyrosine crystals, which are easily identified by their appearance. H. R. LE S.

**Chemistry of Wallerian Degeneration.** By FREDERICK W. MOTT and WAKELIN BARRATT (*Proc. Physiol. Soc.*, 1899, 3—5).—Comparison of the healthy with the degenerated side of the spinal cord in two cases, shows that in the degenerated half more water is present, and there is a larger yield of ethereal extract. The ethereal extract is buttery in consistency, and contains but little phosphorus in proportion to the ethereal extract of the healthy side. The ethereal extract of the healthy side consists chiefly of crystals of protagon. These chemical results confirm those derived from histological examination ; in the degeneration process, lecithin appears to be largely replaced by ordinary fat. W. D. H.

**Toxicology of Phenol.** By G. P. MENEGAZZI (*L'Orosi*, 1898, 21, 325—327).—0.6675 gram of phenol was injected into the rectum of a rabbit ; death occurred in 37 minutes, and the animal was immediately dissected and the phenol extracted according to the method proposed by Jacobson, and recommended by Dragendorff. From the œsophagus, stomach, intestines, and their contents was obtained 0.0928 gram ; from the brain, heart, lungs, liver, spleen, kidneys, muscles, and blood, 0.0878 gram ; and from the urine, 0.0154 gram of phenol. The total amount of phenol extracted, 0.196 gram, forms only 29.2 per cent. of that originally injected, the deficiency being due partly to defective experimental methods, and partly to combination of the phenol with the animal tissues. N. L.

**Physiological and Toxic Action of Methylxanthines and their Influence on Muscular Fatigue.** By VALERIO LUSINI (*L'Orosi*, 1898, 21, 257—263).—Experiments with frogs show that the minimum toxic doses of monomethylxanthine, dimethylxanthine or theobromine, and trimethylxanthine or caffeine are 0.022—0.024, 0.014—0.015, and 0.007 gram per 100 grams of body-weight, whilst the minimum lethal doses are 0.030, 0.020, and 0.012 gram respectively. It is also found, by excitation of the sciatic nerve, and by direct excitation of the gastrocnemius muscle, that the action of these compounds in diminishing the resistance of the muscles to fatigue increases progressively from monomethylxanthine to trimethylxanthine. It therefore appears that the successive introduction of methyl groups into the xanthine molecule is accompanied by an increased toxic and physiological action. N. L.

## Chemistry of Vegetable Physiology and Agriculture.

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**Action of Yeast on Glyceraldehyde and Dihydroxyacetone.** By OTTO EMMERLING (*Ber.*, 1899, 32, 542—544).—Although numerous investigators have stated that the mixture of glyceraldehyde and dihydroxyacetone obtained by the oxidation of glycerol, undergoes fermentation with yeast, yet this ferment is entirely without action on the pure substances. Further, on oxidising glycerol with platinum black, according to Grimaux's method, the product obtained does not evolve carbonic anhydride when treated with yeast, although after heating it for some time at 60°, a slight evolution of the gas is noticeable on adding the ferment; this is probably due to the conversion of some of the glycerose into acrose. J. F. T.

**The Sorbose Bacterium.** By OTTO EMMERLING (*Ber.*, 1899, 32, 541—542. Compare Bertrand, *Abstr.*, 1898, i, 550—556).—Bertrand has stated that the sorbose bacterium has the property of oxidising sorbitol to sorbose, and, further, of converting glycerol into dihydroxyacetone. The author finds that, not only is this correct, but that the fungus grows rapidly when placed in certain articles of food, for instance, beer, covering the surface with a thick leather-like skin, which consists of a mixture of cellulose and a compound analogous to chitin, since, on treatment with hydrochloric acid and extraction with alcohol, it gives a crystalline hydrochloride, similar in form to glucosamine (chitosamine) hydrochloride. J. F. T.

**Production of Fluorescent Pigment by Bacteria.** By EDWIN O. JORDAN (*Proc. Amer. Physiol. Soc.*, 1898, 18—19. *Amer. J. Physiol.*, 2).—Experiments made with six different cultures of 'fluorescent bacteria' show that phosphorus and sulphur are essential for the formation of the pigment. The following organic acidic substances are arranged in fluorescegenic value:—asparagine, succinic, lactic, citric, tartaric, uric, acetic, oxalic, and formic acids. The presence of the methyl or methylene group is thus favourable, but fluorescence is not coincident with dibasicity, or the presence of two  $\text{CH}_2$ -groups as Lepierre asserts. Diffused daylight is unfavourable to pigment production. W. D. H.

**Action of Ethereal Oils on Fungi.** By THOMAS BOKORNY (*Pflüger's Archiv*, 1898, 73, 555—594).—Putrefactive bacteria and moulds were grown on nutritive media, and the amount of various ethereal oils necessary to hinder the growth was determined by adding the oil to the medium.

The terpenes are strongly toxic for moulds, less so for bacteria; their action is due to the diminution of oxidation which they cause. Cymene is a weaker poison. Whereas turpentine hinders the growth of anthrax in a concentration of 1:75,000, cymene in the concentration of 1:7500 does not hinder putrefaction. Aldehydes like

vanillin are toxic also. Oil of valerian owes its poisonous character to isovaleric acid, the mustard oils to the CS:N-group.

W. D. H.

**Digitalis Ferment.** By BRISSEMORET and JOANNE (*J. Pharm.*, 1898, [vi], 8, 481—484).—The statements made by Kosmann (*Abstr.*, 1877, i, 488—489) as to the diastatic properties of digitalis ferment are based on untrustworthy experiments, but those as to its oxidising properties are confirmed. The ferment is probably a constituent of a large number of vegetable substances, and is analogous to the oxidising ferments (oxydases) isolated by Bertrand. Recently dried digitalis leaves contain the ferment, which, however, gradually disappears when the leaves are kept.

H. R. LE S.

**General Progress of Vegetation.** By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Ann. Chim. Phys.*, 1896, [vii], 9, 5—119 and 145—229).—The organic and mineral constituents were determined in seeds and in the corresponding plants at different periods of growth. The determinations were made in roots, stems, leaves, flowers, and seeds. The plants selected were white lupins, wheat, lucerne, and robinia.

*Lupins.*—Seeds sown April 10, 1893; plants analysed May 3 and 25, June 14, July 1, and August 24. By the 3rd of May, there was a slight loss of organic matter; the percentage of carbon in the organic matter remained the same, that of the nitrogen and hydrogen being lower by 1/10th and 1/9th respectively. There was a considerable gain of calcium and potassium, but a loss of phosphoric acid. During the next three weeks, the weight of the plant increased fourfold; the roots amounted to 11·4 per cent. of the whole plant, and contained the greatest amount of mineral matter. The production of carbonaceous was greater than that of nitrogenous substances; the percentages of carbon, hydrogen, and nitrogen were highest in the leaves. The ash constituents, especially potash, increased, more in the stems than elsewhere.

From May 25 to June 14, the increase was again fourfold, and was more in the organic than in the mineral matter, the percentage amount of which actually diminished (from 10·6 to 7·8). The amount of root became relatively less (8·8 per cent.). Ash constituents became most abundant in the leaves. There was a relative increase of carbon (especially in roots and stems).

In the next period (2 weeks), the increase in total weight was slower, and was mainly in the organic matter. The relative composition of the plant (as a whole) remained about the same.

In the last period of two months, during which fructification was completed, the absolute weight diminished by nearly a third, the loss being mainly in the organic matter, but partly in the mineral matter. The amount of root became relatively greater (11·2 per cent.); the leaves, stems, and fruit amounted respectively to 3·7, 40·7, and 44·4 per cent. of the whole plant. The roots contained the least, the leaves the most ash. The relative amounts of carbon and nitrogen were reduced, whilst the oxygen increased.

*Wheat.*—The results were similar to those obtained with lupins.

*Lucerne*.—After three months, the increase was found to be to a great extent in the roots, which amounted to nearly half the plants; the amount of stems was about the same as two months earlier, whilst the leaves diminished in weight.

*Robinia*.—At the time of flowering, the relation of twigs (the new shoots independently of the branches) to leaves is much less than in the case of herbaceous plants. The proportion of mineral matter is about the same as in the same parts of annual plants. At the commencement of fructification, the amount of ash in the different parts does not differ much, but subsequently there is a great accumulation of mineral matter in the leaves.

N. H. J. M.

**Influence of Gases and Vapours on the Growth of Plants.** By EMIL P. SANDSTEN (*Minnesota Bot. Studies*, 1898, [ii], Pt. i, 53—68).—*Oxygen*.—Seeds germinate readily in oxygen, but the seedlings do not grow so rapidly as in air. Growing shoots remain unaltered for as long as 20 days in an atmosphere containing from 25 to 100 per cent. of oxygen, but slowly die when removed.

*Nitrous Oxide*.—Seeds of *Phaseolus multiflorus* and *Vicia faba* failed to germinate in an atmosphere containing 80 per cent. of the gas, but the seeds were not killed, and afterwards germinated in air. Seedlings remained alive in the gas for more than 24 hours, but did not grow. Water plants (*Salvinia natans* and *Philotria*) showed increased growth in solutions saturated with nitrous oxide.

*Ammonia*.—Seeds of *Phaseolus* germinated in presence of gaseous ammonia (1 : 24,000) as freely as in the control experiment. Seeds of *Vicia faba*, however, failed to germinate in presence of less ammonia (1 : 28,000), but with still less ammonia (1 : 32,000), 90 per cent. of the seeds germinated. Both seeds failed to germinate when the amount of ammonia reached 1 in 20,000. The growth of young seedlings of *Zea mais* was retarded when kept for 48 hours in air containing ammonia (1 : 20,000). *Salvinia natans* and *Philotria* were killed by adding 0.1 c.c. of ammonia to 2000 c.c. of the water.

*Chloroform* and *Ether*.—Seedlings of *Zea mais* showed a decided acceleration in growth after being kept in moist air containing chloroform or ether (1 : 10,000); with twice the amount of either vapour, growth is greatly retarded.

*Carbon Bisulphide*.—The smallest trace is injurious to growing plants, but resting seeds are not affected.

*Alcohol* retards growth, and destroys seedlings, when present in amounts exceeding 1 in 10,000; smaller quantities have no effect on the growth of seedlings. Resting bulbs grew in an atmosphere containing one part of alcohol in 1000 to 500, but the floral organs were dwarfed and the buds remained unopened (compare Detmer, Abstr., 1883, 105).

N. H. J. M.

**Relation between the Intensity of the Green Colour of Leaves and the Chlorophyllic Assimilation.** By ED. GRIFFON (*Compt. rend.*, 1899, 128, 253—258).—Whilst dark green leaves were generally found to possess greater assimilating energy than those of a paler green colour (cereals, lettuce, begonia, fuchsia), in some cases leaves of the same tint differed (fuchsias), or pale green leaves

assimilated equally with, or even more than, leaves of a darker colour (peach, plum, chrysanthemum). The thickness and structure of the mesophyll, and the number, size, and tint of the chloroleucites in each cell are conditions which influence the colour of the leaves, either in the same or in different directions, and their action on the decomposition of carbonic anhydride gives a resultant, the nature and extent of which remains to be ascertained. In some cases, this resultant seems to be in opposition to the data furnished by anatomy. Other causes, possibly the individual activity of the chromoleucites, or the different natures of the chlorophylls, produce differences in assimilation.

N. H. J. M.

**Life-history of Starch Grains in Higher Plants.** By ARTHUR MEYER (*Bied. Centr.*, 1899, 28, 118—120; from *Untersuchungen über die Stärkekörner*, Jena, 1895; and *Bot. Centr.*, 1897, 69, 208).—So-called starch solutions may be considered as a mixture of water and drops of a viscous solution of water in starch (amylous water-solution); iodine-starch is probably a well defined solution of iodine in starch.

The action of diastase on amylose is probably catalytic, the amylose taking up the elements of water and breaking up into two or more molecules of amyloextrin, the latter decomposing with formation of dextrin and isomaltose. Dextrin yields maltose, which is also produced by intramolecular migration from isomaltose.

Starch grains are sphæro-crystals, porous, like those of inulin and amyloextrin; they absorb about the same amount of glycerol as of water. Starch grains are never produced in the cytoplasm or in the cell sap, but grow from the beginning in a chromatophore. In chlorophyll grains, it seems to be the stroma alone which produces starch, and also diastase.

When abundant production of starch is taking place in leaves, the amount of diastase is relatively small, whilst with vigorous solution of starch the amount of diastase is high. Maltose, the last product of the decomposition of starch by diastase, can be detected in leaves.

Formation of layers is due to the unequally rapid deposition of starch. In the case of *Pellonia* and *Adoxa*, it was observed that thick, dense layers of starch were formed in the daytime, thin, loose layers in the night.

The author agrees with Berthold in considering protoplast as an emulsion essentially similar to an amylous water-solution, a more or less viscous solution of a relatively small amount of water in a substance which, in a liquefied condition, is not miscible with water.

N. H. J. M.

**Assimilation of Carbohydrates and Elaboration of Organic Nitrogen by Higher Plants.** By MAZE (*Compt. rend.*, 1899, 128, 185—187).—Narbonne vetches were allowed to germinate in the dark, and out of contact with microbes, and when the seedlings were from 8 to 10 cm. long they were placed in solutions containing, in 1000 c.c., 1 gram of potassium phosphate, 1 gram of sodium nitrate, 2 grams of calcium carbonate, 0.2 gram of a mixture of

magnesium sulphate, ferrous sulphate, and manganese chloride, and traces of zinc chloride, with from 10 grams to 60 grams of glucose. The plants were then left in the dark from 39 to 92 days. It was found that, after 92 days, the plant in the solution containing 40 grams of glucose per litre had increased in dry weight by 635.4 milligrams above the weight of the seed, whilst a plant in the solution containing 60 grams of glucose had increased by 507.2 milligrams. Plants placed under similar conditions in similar solutions containing no glucose, were found, at the end of 53 days, to weigh considerably less than the seed. The plants grown in the glucose solutions showed normal and well developed roots, whilst the total length of the stalk and its branches exceeded 1.5 metres; the leaves have a parchment-like appearance, and the folioles remain closed. Nitrates could be found in the stalks up to about the last internode. It follows that higher plants, like plants containing no chlorophyll, can live out of contact with light at the expense of compounds already elaborated. Under normal conditions, they derive their food from the much simpler compounds which result in the main from the action of bacteria and moulds on the complex organic compounds present in the soil.

C. H. B.

**Influence of Carbohydrates on the Formation of Proteids in Plants.** By ERNST SCHULZE (*Chem. Centr.*, 1898, ii, 667—668; from *Landw. Jahrb.*, 27, 516—520).—Whilst Hansteen's results (*Abstr.*, 1898, ii, 179) with *Lemna minor*, supported Pfeffer's theory of the effect of carbohydrates on the regeneration of proteids from asparagine, the author pointed out that both in the above-ground and underground portions of plants considerable accumulations of asparagine occur along with abundance of starch or sugar; and he showed that seedlings (*Lupinus luteus*) which had accumulated asparagine during 10 days in absence of light continued to accumulate asparagine as well as proteids when exposed to light, whilst the other nitrogenous non-proteids diminished in quantity. To reconcile the author's observations with Pfeffer's theory, Borodin suggested that, not carbohydrates generally, but only glucose, is effective in the production of proteids from asparagine, an assumption which is supported by Hansteen's results with *Lemna minor*, which showed that proteids were formed from asparagine in presence of grape sugar, but not with cane sugar.

The results of recent experiments with a number of different seedlings which had been grown for two weeks or more in the dark, showed that the loss of proteids was least the greater the amount of non-nitrogenous matter present. In the changes which these substances undergo in the seedlings, soluble carbohydrates are formed from insoluble substances, a portion being converted into glucose. The glucose promotes the regeneration of proteids from asparagine, glutamine and perhaps other products of the decomposition of protein. Regeneration of protein is greatest in the case of seeds which contain the most non-nitrogenous reserve substances, but the decomposition of proteids is not checked by the presence of non-nitrogenous compounds.

N. H. J. M.



**Formation of Proteids and the Assimilation of Nitrates by Phanerogams in the Absence of Light.** By U. SUZUKI (*Bul. Coll. Agr. Imp. Univ. Tokyo*, 1898, 3, 488—507. Compare *ibid.*, 2, No. 7).—Kinoshita (Abstr., 1896, ii, 54) found that ammonium salts yield asparagine, nitrates being stored up, whilst, according to Hansteen (*Ber. deut. bot. Ges.*, 1896, 14, 368), nitrates are but little assimilated in darkness. Ishizuka's experiments with a number of plants indicate that in darkness the nitrates stored up in the roots gradually decrease, whilst the amount of asparagine increases (*Tokyo Bul.*, 1897, 2, 471). Godlewski concluded (Abstr., 1897, ii, 583) that nitrates are assimilated in the dark, with production of asparagine, but not of proteids; whilst Laurent (*Bul. Acad. roy. Belg.*, 1896, 32, No. 2) maintains that neither ammonium salts nor nitrates are assimilated in absence of light.

The author's first experiments failed to show any assimilation of nitrates in the dark, but by increasing the amount of sugar from 1 to 10 per cent., very decided evidence of such assimilation was obtained. The experiments were made with barley, *Phaseolus multiflorus*, and potatoes.

In total darkness, the plants produced proteids from nitrates in presence of a sufficient amount of sugar in the plant cells; with insufficient sugar, no assimilation occurred. This accounts for some of the divergent results obtained by others.

The intermediate product, between nitrates and proteids, is most probably asparagine; this accumulates under conditions unfavourable to the production of proteids.

Zuleski's recent results also show the possibility of protein formation in darkness (*Ber. deut. bot. Ges.*, 1897, 15, 536). N. H. J. M.

[Chlorine, Phosphorus, and Sulphur in Plants]. By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 17—23, 23—26).—See this vol., ii, 327, 330.

**Occurrence of Copper in the Plant World.** By GEORGE B. FRANKFORTER (*Chem. News*, 1899, 79, 44—45).—A dead oak, at Minneapolis, was observed to have flakes of metallic copper disseminated through the pores of the wood, but particularly in the more recent annual rings. The ash from samples representing the whole tree contained 0·0012 per cent. of copper, the ash of the heart wood 0·0008 per cent., of the wood near the bark 0·00395 per cent., and of the wood midway between the bark and heart 0·00186 per cent. The powdery, cuprififerous deposit itself contains 95·01 per cent. of copper, which is mostly in the metallic state, but associated with a white, crystalline substance not yet examined thoroughly. D. A. L.

**Physiological Importance of Arsenic in Vegetation.** By JULIUS STOKLASA (*Chem. Centr.*, 1898, ii, 43; from *Zeits. landw. Versuchsw. Oesterr.*, 1898, 1, 155—193).—The application of superphosphate and ammonium and potassium sulphates as manures introduces much more arsenic into the soil than is generally supposed. One hundred-thousandth of the mol. wt. of arsenious anhydride (in grams per 1000 c.c. of nutritive solution) has a distinct effect on plants,

whilst 1/1000 of the mol. wt. of arsenic anhydride is poisonous. Arsenic cannot replace phosphorus in vegetation.

The toxic effect of arsenious and arsenic anhydrides is manifested, especially with the phanerogams, in its disturbing effect on the activity of the chlorophyll. The destruction of living molecules is much more rapid in the chlorophyll apparatus than in the protoplasm of the plant cell.

Superphosphate contains 0.012—0.26 per cent. of arsenic ; injury to plants was found to take place only when the manures contained over 0.4 per cent. of arsenic.

N. H. J. M.

Oil from the Rhizome of *Aspidium Filix mas*. By JULIUS KATZ (*Arch. Pharm.*, 1898, 236, 655—662).—This oil consists of the glyceric salts of oleic, palmitic, and cerotic acids, the chief constituent being triolein. The amount of palmitic and cerotic acids is only some 4.5 per cent. ; a small amount of butyric acid is also present.

J. J. S.

Chemical and Physical Characters of some Indian Edible Oils. By ARTHUR W. CROSSLEY and HENRY R. LE SUEUR (*J. Soc. Chem. Ind.*, 1898, 17, 989—994).—Oils from the following plants have been examined:—Liquid oils.—*Amora rohituka*, *Anacardium occidentale*, *Arachis hypogea*, *Argemone mexicana*, *Brassica alba*, *B. campestris*, *B. juncea*, *B. napus*, *B. nigra*, *Carthamus tinctorius*, *C. oxyacantha*, *Erica sativa*, *Guizotia abyssinica*, *Juglans regia*, *Lepidium sativum*, *Linum usitatissimum*, *Luffa egyptica*, *Nigella sativa*, *Olea europea*, *Papaver somniferum*, *Prunus armeniaca*, *Raphanus sativus*. Solid oils.—*Bassia latifolia*, *B. butyracea*, *Buchanania latifolia*, *Cocos nucifera*, *Garcinia indica*, *Vateria indica*. In most cases, the following data are given:—Sp. gr. at 15.5°, acid value, saponification value, iodine value, Reichert-Meissel value, insoluble fatty acids, optical activity in 20 cm. tube, viscosity, and refractive index. A list is also given of the uses to which these oils are put in India.

J. J. S.

Chemical Constituents of Cork. By HERMANN THOMS (*Chem. Centr.*, 1898, ii, 1102—1103 ; from *Pharm. Centr. H.*, 39, 699—700).—By extracting 10 kilograms of finely-divided cork with ether and evaporating, 475 grams of a rather sticky residue is obtained, from which cold ether dissolves vanillin and a waxy substance, cork-wax ; the latter, when hydrolysed with alcoholic potassium hydroxide solution, yields an acid and an alcohol. From the residue of the ethereal extract which is not dissolved by cold ether, *cerin*,  $C_{30}H_{50}O_2$  or  $C_{32}H_{54}O_2$ , is obtained by boiling it with 5 per cent. sodium carbonate solution, then with 5 per cent. potassium hydroxide solution, and drying the insoluble residue ; it crystallises from ethylic acetate in lustrous needles, melts at 249°, and is soluble in the ordinary solvents. Its solution in acetic anhydride gives a pink coloration with concentrated sulphuric acid, and its solution in chloroform when shaken with an equal volume of concentrated sulphuric acid, becomes first yellow, and then, after several hours, changes to violet. Cerin belongs to the phytosterols, and yields acetyl and benzoyl derivatives.

E. W. W.

**Occurrence of Tyrosine, Leucine, and Asparagine in the Pod of the Broad Bean.** By EMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm.*, 1898, [vi], 8, 385—390).—The darkening of the pod of the broad bean at maturity is due to the presence of two oxidisable substances (*chromogens*), one of which oxidises spontaneously on exposure to the air, the other only under the influence of an oxidising ferment (oxydase). The episperm and kernel of the bean contain no oxidisable chromogen. Tyrosine, leucine, and asparagine are shown to be present in the solution obtained by the extraction of the pod with alcohol; the oxidisable chromogens are also soluble in it. The author concludes that tyrosine is the principal oxidisable chromogen. H. R. LE S.

**Occurrence of Strophantin in the Algerian Oleander.** By DUBIGADOUX and DURIEU (*J. Pharm.*, 1898, [vi], 8, 433—434).—The substance obtained by mixing the dry powdered latex with chalk, lixiviating with alcohol (95°), and recrystallising the residue left on spontaneous evaporation of the solution, is shown from a comparison of its properties with those of an authenticated specimen to be identical with strophantin. H. R. LE S.

**Poisonous Effect of Sodium Nitrate.** By FRIEDRICH KRÜGER and G. BERJU (*Chem. Centr.*, 1898, ii, 936; from *Centr. Bakt. Par.*, 4, ii, 674—683).—The injurious effect on plants of large amounts of sodium nitrate, and the extremely poisonous action of perchlorate observed by Sjollem (Abstr., 1897, ii, 585) and Maercker are confirmed by the authors' experiments. The peculiar bending of the plants seems, however, to be produced by an excess of pure sodium nitrate alone, as well as by perchlorate.

The poisonous symptoms and deformity produced by nitrate and perchlorate have nothing to do with the disease caused by *Rhynchosporium graminicola* Heinsen. N. H. J. M.

**Analysis of Plants and Soil and the Estimation of the Quality of a Soil.** By ZDZISLAW JANUSZEWSKI (*Bied. Centr.*, 1899, 28, 77—79; from *Inaug. Diss. Leipsic*, 1895).—Field experiments on wheat were conducted at two different farms; samples of the soil being in each case submitted to mechanical separation, and the constituents soluble in 10 per cent. hydrochloric acid determined. The total nitrogen and the phosphoric acid were determined in the produce, both grain and straw. There were, in each case, five pairs of plots, (1) with manure, (2) with nitrogen alone, (3 to 5) nitrogen, together with with different amounts of phosphoric acid.

It is concluded that the analysis of the grain, but not of the straw, gives very useful indications, especially as regards phosphoric acid. But a knowledge of the composition of the best specimens of the plant obtainable is alone insufficient, as an excess of some constituent may influence the amounts of others which are taken up. When a plant contains the maximum amount of one constituent, it is to be concluded that this constituent is present [in the soil] in sufficient quantity; but a minimum amount of any constituent in a plant may be due to various causes. Plant analysis, therefore, should only be employed for estimating the quality of a soil, in conjunction with manure experiments. N. H. J. M.

## Analytical Chemistry.

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**Iodometry.** By JULIUS WAGNER (*Zeit. anorg. Chem.*, 1899, 19, 427—453).—The author has determined the accuracy of the estimation, by means of thiosulphate solutions, of the iodine liberated from acidified potassium iodine solutions when the oxidising agents employed are potassium and sodium bromate, potassium dichromate, potassium chromate, and potassium di-iodate. The use of a 2—3 per cent. solution of starch is recommended as indicator, and no benefit is obtained by using more expensive preparations such as ozonised starch. The titrations must be carried out in flasks and not in beakers; a titration with potassium dichromate and potassium iodide required 25.67 c.c. of thiosulphate when carried out in a flask and three titrations varied by only 0.01 c.c.; a similar titration in a beaker required 25.52 c.c. of thiosulphate, and three titrations varied as much as 0.07 c.c.

A comparison of the results obtained by these oxidising agents shows that potassium dichromate gives results which are 0.3 per cent. higher than those obtained by any of the other salts; and this value is not altered by a further purification of the salts. This high result is due to the catalytic action of potassium dichromate effecting an oxidation of the hydrogen iodide by the air, for the difference in the titration of solutions containing air and those from which the air is expelled by a current of carbonic anhydride amounts to from 0.2 to 0.5 per cent., whereas no difference can be detected in solutions saturated with air as compared with those free from air when potassium di-iodate is the oxidising agent. The author points out that the low values obtained for the atomic weight of chromium by iodometric methods are due to this cause (Meineke, *Annalen*, 1891, 261, 339).

Potassium dichromate may be employed for absolute determinations under known conditions; it is very easily purified by crystallisation, and should be finely powdered and dried at 100°, but it is quite unnecessary to fuse it. Potassium di-iodate gives accurate results, and is easily purified by crystallisation, either alone or with the addition of a small quantity of iodic acid to convert any iodate which may be present into di-iodate. Potassium iodate, potassium bromate, and sodium iodate give accurate results when purified by recrystallisation, or their value may be determined by a thiosulphate solution standardised by means of pure potassium di-iodate. Sodium bromate is difficult to obtain in a pure state, and, owing to its solubility, not easily purified by recrystallisation; by precipitating the aqueous solution with alcohol, a fairly uniform product is obtained, but for accurate work it must be standardised against one of the above salts.

E. C. R.

**Iodometric Estimation of Alkalis and Acids.** By CLAUDE F. WALKER and DAVID H. N. GILLESPIE (*Zeit. anorg. Chem.*, 1899, 19, 194—203).—Methods for the estimation of alkalis and acids based on

the reactions expressed in the equations,  $6\text{ROH} + 3\text{I}_2 = \text{RIO}_3 + 5\text{RI} + 3\text{H}_2\text{O}$ , and  $\text{RIO}_3 + 5\text{RI} + 3\text{H}_2\text{SO}_4 = 3\text{I}_2 + 3\text{R}_2\text{SO}_4 + 3\text{H}_2\text{O}$ , have been previously employed by Gröger (Abstr., 1894, ii, 251) and Phelps (Abstr., 1896, ii, 673). Great care must be taken to exclude carbonic anhydride during the analysis; the alkali solution contained in a closed flask, provided with an absorption apparatus to arrest any iodine which may volatilise, is treated with a known excess of iodine solution and boiled for a short time to decompose hypiodites, then cooled and the excess of free iodine titrated with arsenious acid. The results obtained with solutions of barium and potassium hydroxides are accurate, and are not influenced by the amount of alkali employed or by the amount of iodine in excess. A modified method of procedure is as follows: the alkali solution is allowed to flow into an excess of iodine solution contained in an Erlenmeyer flask, and the mixture boiled until all traces of free iodine are volatilised. The remaining liquid, which consists of a neutral mixture of iodate and iodide, is cooled, mixed with a slight excess of sulphuric or hydrochloric acid, and the liberated iodine titrated with thiosulphate solution. The results are very fairly accurate, although slightly lower than those obtained by Gröger's or the gravimetric methods.

The estimation of hydrochloric or sulphuric acid by this method is effected by adding the acid to a known excess of alkali, and then proceeding as above.

Alkali carbonates cannot be estimated by this method.

E. C. R.

**Presence and Estimation of Chlorine in Plants.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 23—26).—When plants are carefully incinerated, a considerable part of the carbon being left unburnt, and the residue is treated with dilute nitric acid, the quantity of chlorine obtained is too low. An accurate estimation can be made by burning the dried substance in excess of oxygen, and passing the products over red hot sodium carbonate. The differences are, however, not so great as in the case of sulphur and phosphorus, unless, during incineration, the temperature is raised to a red heat. Attempts to distinguish between total chlorine and organic chlorine, by treating the plant with dilute nitric acid and precipitating with silver nitrate, did not yield conclusive results. In all cases, the quantity of chlorine is more than sufficient to combine with all the sodium, although the difference varies in different parts of the plant, and hence it cannot be assumed that all the chlorine enters the plant in the form of sodium chloride.

C. H. B.

**Detection of Perchlorate in Chili Saltpetre.** By NYSSENS (*Chem. Centr.*, 1898, ii, 1281; from *Bull. Assoc. Belge*, 1898).—The perchlorate is present in the Chili saltpetre as the sparingly soluble potassium salt. A weighed quantity of the Chili saltpetre is treated with 15 c.c. of a saturated solution of potassium perchlorate, and the tube containing the mixture is placed in water of the temperature of the laboratory. The saltpetre and all the soluble impurities dissolve, except the perchlorate; the insoluble matter is then collected on a filter and examined, after being washed once with the perchlorate

solution and once with alcohol. If crystals of potassium perchlorate are present, the usual quantitative process should be applied.

L. DE K.

**Estimation of Perchlorate in Alkali Nitrates.** By N. BLATTNER and J. BRASSEUR (*Chem. Zeit.*, 1898, 22, 589—590).—Five to ten grams of the dry and finely powdered sample, the amount of chlorine as chloride in which has been accurately determined, is carefully mixed with 8—15 grams of calcium hydroxide which is free from chlorine, and ignited for 15 minutes in a covered porcelain crucible. The addition of lime prevents the mass from melting, and, therefore, the perchlorate is reduced to chloride at a moderate temperature; the mass, moreover, can readily be transferred from the crucible to a beaker, where it is dissolved in dilute nitric acid, and the chlorine again estimated gravimetrically or by titration, after neutralising the acid by calcium carbonate; the increase corresponding with the perchlorate present. If the amount of silver chloride is very small, it may be dissolved off the filter with dilute ammonia, and evaporated to dryness in a tared dish.

L. DE K.

**Separation of Bromine, Chlorine, and Iodine in the form of Silver Salts.** By HENRI BAUBIGNY (*Compt. rend.*, 1899, 128, 51—54).—The separation of chlorine and bromine from iodine, when they are in the form of mixed silver salts, by the action of sulphuric acid and potassium dichromate (this vol., ii, 244), is applicable also to silver salts that have been dried at a moderately high temperature; the weight of the mixed salts, therefore, can be ascertained before they are treated further. Bromine and chlorine in the form of silver salts cannot, however, be separated satisfactorily by any method of differential oxidation. The best plan is to slightly acidify the alkaline liquid in which the chlorine and bromine have been condensed, in the process of separating them from the iodine, allow time for the sulphurous acid present to reduce any oxygen compounds of bromine and chlorine, again make alkaline, add permanganate until a permanent pink coloration is obtained, and afterwards separate the chlorine and bromine by the cupric sulphate and permanganate method (*Abstr.*, 1898, ii, 90, 137).

In order to detect bromine in a mixture of haloid silver salts, the precipitate is mixed with a small quantity of nitric acid of sp. gr. = 1.34, and a few crystals of potassium permanganate are added. The silver iodide is converted into iodate, and the chloride is not affected, but any bromine present is liberated, and can be detected by its action on fluorescein paper (*ibid.*, 138).

C. H. B.

**Analysis of Organic Substances containing Sulphur and Halogens.** By ANTONIO LONGI (*Gazzetta*, 1898, 28, ii, 247—252).—The author describes the determination of sulphur and halogens in volatile organic compounds, using an apparatus which he has recently devised for estimating sulphur in illuminating gas (*Abstr.*, 1898, ii, 535). Numerous test analyses show that the method gives good results.

T. H. P.

**Aræometric Valuation of Crude Sulphur.** By PAUL FUCHS (*Zeit. angew. Chem.*, 1898, 1189—1190).—Fifty grams of the sulphur are dissolved in 200 grams or 158 c.c. of carbon bisulphide, and the sp. gr. of the liquid taken with a specially constructed hydrometer devised by the author; the degrees on the stem multiplied by four represent the percentage of pure sulphur in the sample.

It is necessary to first test the solvent alone, and, if needful, to make a correction. A table for temperature corrections is given; also one showing the exact relation between the sp. gr. and percentage of sulphur in solutions of the latter in carbon bisulphide. L. DE K.

**Estimation of Sulphur and Alkalis in Liver of Sulphur.** By LÉONCE BARTHE (*J. Pharm.*, 1898, [vi], 8, 533—537).—The following method for the estimation of sulphur in a solution of the polysulphides of the alkalis in the absence of alkaline earths is based on the oxidising power of nascent bromine. To 1—2 c.c. of the solution are added 10 c.c. of a concentrated solution of pure soda or potash, 25 c.c. of distilled water, and 30 c.c. of a solution of sodium hypobromite. The liquid is heated to boiling, and dilute hydrochloric acid added, the heating and addition of acid being continued until all the free bromine is expelled and the liquid has become viscid. The sulphuric acid thus formed is estimated in the usual manner as barium sulphate. Since the pharmaceutical preparations of liver of sulphur are free from the alkaline earths, the estimation of the alkalis is readily effected thus: to 2 c.c. of the solution are added 20 c.c. of distilled water and 5 c.c. of concentrated sulphuric acid; the liquid is boiled, filtered through a double filter paper, the filtrate evaporated in a tared capsule, incinerated, and weighed. This gives the weight of mixed sulphates, and by dissolving these in water and precipitating with a barium salt, the total amount of sulphuric acid is determined; from the two results thus obtained, the relative amounts of sodium and potassium are readily calculated. H. R. LE S.

**Estimation of Sulphuric Acid in the Presence of Iron.** By GEORG LUNGE (*Zeit. anorg. Chem.*, 1899, 19, 454—456).—A criticism of the method described by Küster and Thiel (this vol., ii, 247). E. C. R.

**Estimation of Nitric Acid.** By WILHELM ACKERMANN (*Chem. Zeit.*, 1898, 22, 690—691).—The process is based on the fact that nitrates yield their nitrogen as ammonia when boiled with ferrous sulphate and aqueous soda. To get trustworthy results, it is necessary to work under definite conditions.

The nitrate solution is made by dissolving 20 grams of the sample in water and diluting to one litre, 50 c.c. being used for the experiment; the solution is put into a 500 c.c. flask, 130 c.c. of a solution of ferrous sulphate (308 grams dissolved to 1 litre) added, and then 30 c.c. of aqueous soda of sp. gr. = 1.33; to prevent bumping, a little reduced iron is also added. The distillation is commenced at once and usually, after about half an hour's boiling, the distillate will be quite free from ammonia, but if this keeps on coming over almost to the last, the experiment cannot be trusted. The distillate is, as usual, collected in

a receiver containing a known volume of standard acid, the excess of which is titrated, using litmus as indicator. The reagents must be free from ammonia and nitrates. The process may be applied to manures, if the phosphoric acid is first converted into calcium phosphate by adding a slight excess of calcium chloride, followed by the aqueous soda and the ferrous sulphate; if this precaution be not taken, the reduction of the nitrate will be very much retarded and the process will not give satisfactory results.

L. DE K.

**Estimation of Phosphorus and Sulphur in Plants and Plant Ashes.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 17—23).—Experiments made with *Cynosurus cristatus* show that the quantity of phosphoric acid or sulphuric acid obtained by digesting the plant with cold dilute nitric acid, or by carefully incinerating it, is always lower than that obtained by burning the dried plant in a current of oxygen and passing the products of combustion over sodium carbonate at a low red heat. The results obtained by projecting a mixture of the substance with five times its weight of potassium nitrate into a red-hot porcelain crucible are also lower than those given by the oxygen and sodium carbonate method, although the differences are not so great as in the other cases. The general results indicate that a considerable proportion of the phosphorus and sulphur exist in the plant in the form of organic compounds and not in combination with metals. This proportion varies in different parts of the same plant.

In order to obtain accurate results, combustion of the vegetable matter must always take place in presence of an excess of oxygen, the temperature must be sufficiently high, and there must be an excess of sodium carbonate; if these conditions are not satisfied, there may be loss of both phosphorus and sulphur in one form or another

C. H. B.

**Reynoso's Method for the Analysis of Phosphates.** By UBALDO ANTONY and G. H. MONDOLFO (*Gazzetta*, 1898, 28, ii, 142—147).—This method of separating the phosphate radicle from the alkaline earth metals and from iron, aluminium, &c., consists in treating the phosphate with concentrated nitric acid in presence of tin, the phosphate residue forming, with the metastannic acid, an insoluble compound, the metals from the phosphate precipitate remaining in the liquid. Some of the tin may, however, dissolve, and some of the metals may remain in the precipitate. The authors show that these disadvantages may be avoided by treating the phosphate precipitate with 77 per cent. nitric acid (sp. gr. = 1.427), and they give a modified method of testing the filtrate for iron, aluminium, &c. They have examined the insoluble compounds formed by metastannic acid with the phosphate radicle and with iron, but have arrived at no definite conclusions as to their composition.

T. H. P.

**Volumetric Citrate-process for the Rapid and Accurate Estimation of Phosphoric Acid in Superphosphates.** By SIGISMUND LITTMAN (*Chem. Zeit.*, 1898, 22, 691—693).—Ten grams of the superphosphate is shaken for half-an-hour with 400 c.c. of water



contained in a 500 c.c. flask, which is then filled up to the mark, and the solution filtered. To 50 c.c. of the filtrate,  $N/10$  soda is added until the liquid turns distinctly yellow, methyl-orange being used as indicator. The liquid now contains unaltered superphosphate and monosodium phosphate, and the former is converted into the latter by adding 10 c.c. of a solution of sodium citrate; this is prepared by carefully neutralising a solution of 30 grams of sodium hydroxide with a strong solution of citric acid, using phenolphthalein as indicator, and then diluting to 250 c.c. The mixture is now titrated with  $N/10$  soda, using phenolphthalein as indicator; this operation requires practice, as the liquid is neutral just before a faint red is noticed. It is therefore advisable to again destroy the colour by  $N/10$  sulphuric acid. Phosphates which contain much iron and aluminium give some trouble, but by first diluting with about 5 times the bulk of water the methyl-orange colour can be more easily observed; a second experiment is then made without dilution, using only phenolphthalein and sodium citrate, subsequently allowing for the soda required by the methyl-orange. Two mols. of sodium hydroxide represent 1 mol. of phosphoric anhydride, and the percentage in the sample is found by multiplying the number of c.c. of soda used by 0.71. Fifty test experiments are given, showing the process to be a good commercial one. L. DE K.

**Estimation of Citrate-soluble Phosphoric Acid in Basic Slags.** By J. FREUNDLICH (*Chem. Zeit.*, 1898, 22, 974—975).—Wagner's latest proposal is to treat the basic slags with a 2 per cent. solution of citric acid, and precipitate with an ammoniacal solution of magnesium citrate. The author has frequently noticed that the liquid turns blackish, and that the ignited phosphate has a reddish colour; this is caused by the samples containing iron sulphide. In contact with citric acid, the latter dissolves with liberation of hydrogen sulphide, and is partially reprecipitated on neutralising the liquid. The author recommends boiling with a little nitric acid before adding the magnesium mixture. L. DE K.

**Estimation of Boric Acid.** By FRANK A. GOOCH and LOUIS C. JONES (*Amer. J. Sci.*, 1899, [iv], 7, 34—40, and *Zeit. anorg. Chem.*, 19, 417—426).—The authors have re-investigated the process devised by Gooch, which consists in distilling the borate with methylic alcohol in the presence of acetic or nitric acid, collecting the distillate in a receiver containing a known weight of calcium oxide, drying, and re-igniting; the increase in weight giving the amount of boric anhydride.

If nitric acid is used, the lime should be very gradually heated, as otherwise there will be loss by spiriting, but if the quantity of nitric acid is regulated by using phenolphthalein as indicator there is no such danger. The conclusion arrived at is that the method is accurate, but this cannot be said of the process proposed by Thaddéeff (*Abstr.*, 1897, ii, 597), in which the distillate is collected in potash solution and the boric acid estimated as potassium borofluoride; an operation attended by a serious loss of boric acid.

The calcium oxide may, however, be replaced with great advantage by sodium tungstate; this should be fused with a slight excess of

tungstic acid so as to remove traces of carbonic anhydride. A weighed quantity of the compound is dissolved in water and placed in the receiver, cooled by ice and trapped with water; after half-an-hour, the liquid is transferred to the dish in which the tungstate was heated, and weighed, evaporated to dryness, and reignited. The apparatus is practically the same as that originally proposed, the retort being made from a 150 c.c. pipette and has the advantage that particles of the residue thrown up during distillation are easily removed from the side of the vessel by a rotatory motion of the retort. The test-analyses show the method to be a practical one.

L. DE K.

**Volumetric Estimation of Boric Acid.** By LOUIS C. JONES (*Amer. J. Sci.*, 1898, 7, 147—153).—The new process is based on the fact that boric acid does not liberate iodine from a mixture of potassium iodide and iodate.

The solution to be tested, which should be distinctly acid to litmus (any large excess of hydrochloric acid should be first neutralised with aqueous soda), is mixed with 5 c.c. of a 10 per cent. solution of barium chloride, and a very slight excess of the usual iodide-iodate mixture, containing a little starch, is added. The strong mineral acid is then neutralised, and the iodine set free is converted into neutral sodium iodide and tetrathionate by carefully bleaching the liquid with a weak solution of sodium thiosulphate.

The boric acid is now in the free state. Phenolphthalein is added, and  $N/5$  solution of soda is run in until the liquid is dark red; a little mannitol is added, which bleaches the liquid, and then more soda and again more mannitol until the colour is permanent. As a rule, 1 or 2 grams of mannitol will be enough for an estimation, and the boric anhydride is then calculated by assuming that, under these conditions, 1 mol. of the acid requires 2 mols. of sodium hydroxide.

The test analyses, including an analysis of colemanite, are very satisfactory; the process is not influenced by the presence of carbonates, silicates, or fluorides.

L. DE K.

**Estimation of Carbonic Oxide, Methane, and Hydrogen by Combustion.** By LOUIS M. DENNIS and CYRIL G. HOPKINS (*Zeit. anorg. Chem.*, 1899, 19, 179—193).—The method consists essentially in gradually adding the oxygen or air for the combustion to the mixture of combustible gases in such a manner that the combustion is effected slowly and regularly by means of a spiral of platinum wire maintained at a red heat by the electric current. The sample of gas to be analysed is transferred to a Hempel's gas pipette, which is connected with a Hempel's burette containing the oxygen; the latter is then gradually allowed to flow into the pipette and the platinum wire in the pipette is heated to redness. When the combustion is complete, the remaining gas is transferred to the burette and measured. By this method, the production of oxides of nitrogen during the combustion is prevented. A sketch of the apparatus is given, and also the details of analysis of carbonic oxide, methane, and hydrogen, and of a mixture of the three gases. The results obtained are accurate.

E. C. R.

**Estimation of Traces of Carbonic Oxide in Air.** By MAURICE NICLOUX (*Ann. Chim. Phys.*, 1898, [vii], 14, 565—574. Compare Abstr., 1898, ii, 536 and 537).—The paper contains details of an analytical method previously described. G. T. M.

**Estimation of Carbon Bisulphide.** By ALWIN GOLDBERG (*Zeit. anorg. Chem.*, 1899, 75—80).—When carbon bisulphide is heated with alcoholic ammonia, at 60° under pressure, one-half of its sulphur is converted into ammonium sulphide which may then be accurately titrated with zinc solution. The best results are obtained if for every gram of carbon bisulphide 5 c.c. of strong ammonia and 25 c.c. of absolute alcohol are used; aqueous ammonia may also be employed, but in that case the process requires several days. The contents of the flask, which should be yellow, are largely diluted with water, excess of standard ammoniacal zinc solution is added, and the liquid heated to boiling. The excess of zinc is then titrated with a standard solution of sodium sulphide, using sodium nitroprusside as indicator. To estimate carbon bisulphide vapour in gaseous mixtures, these are passed through Peligot tubes containing alcoholic ammonia.

A technical process for the estimation of carbon bisulphide in crude benzene is described, based on the diminution in volume by the action of alcoholic ammonia, a duplicate experiment being made with alcohol alone. Brine of sp. gr. = 1.2 is then added to both, the difference in volume representing the carbon bisulphide.

Attempts to isolate the sulphur by the action of hydroxylamine were fairly successful, but unless the amount of carbon bisulphide is already approximately known, the results are not trustworthy, as they depend on the amount of hydroxylamine added. L. DE K.

**Estimation of Potassium and Sodium in the Urine.** By WILMOT PARKER HERRINGHAM (*J. Physiol.*, 1899, 23, 497—498).—One hundred c.c. of urine are evaporated to dryness with 5 grams of ammonium sulphate, and the residue treated with a few drops of sulphuric acid and heated in a platinum capsule until quite white. The ash is then dissolved in boiling water containing a little hydrochloric acid, and to the boiling liquid barium chloride is added. After filtering off the precipitated barium sulphate, the liquid is made alkaline with ammonia, and again filtered; the filtrate is treated with a slight excess of sodium hydroxide, and the excess of barium precipitated by addition of sodium carbonate. The liquid, which now contains the salts as chlorides, together with the excess of sodium hydroxide and free ammonia, is heated to remove the latter, neutralised with hydrochloric acid, and the potassium estimated as platinochloride in the usual way. The sodium is estimated by deducting from the weight of the total chlorides the weight of the potassium chloride and of the sodium chloride formed from the known amounts of sodium compounds added. W. D. H.

**Volumetric Estimation of Lead Dioxide by an Alkaline Solution of Arsenious Acid.** By C. REICHARD (*Chem. Zeit.*, 1898, 22, 774—775).—Lead dioxide is reduced by boiling it with a solution of arsenious acid in sodium hydroxide; an aqueous or ammoniacal solu-

tion has no action. For a successful quantitative test, 0.1 gram of the finely-powdered sample is introduced into a flask with a little water, and after shaking the mixture, 4 c.c. of an alkaline solution of arsenic containing 0.0099 gram of arsenic trioxide per c.c. is added; the liquid is then boiled, and strong solution of soda added, until the brown dioxide has completely dissolved. The solution, diluted with water, is acidified with dilute sulphuric acid and titrated with standard permanganate. If the excess of arsenious anhydride is to be estimated by standard iodine solution, the liquid is first neutralised, then mixed with excess of sodium hydrogen carbonate, filtered hot, and when cold titrated in the usual way.

One mol. of arsenic trioxide corresponds with 2 mols. of lead dioxide.

L. DE K.

### Volumetric Estimation of Cerium and its Applications.

By ANDRÉ JOB (*Compt. rend.*, 1899, 128, 101—102).—The author finds that, in the well-known reaction with hydrogen peroxide, 2 molecules of a ceric salt decompose 1 molecule of hydrogen peroxide; a ceric salt in an acid solution, therefore, can be accurately estimated by means of hydrogen peroxide. Cerous salts can be completely oxidised to ceric salts by treating them, at the ordinary temperature, with lead peroxide and an excess of concentrated nitric acid; but with dilute acid the change is not complete even on heating.

The accuracy of the results is not affected by the presence of thorium, lanthanum, and didymium, so that cerium can be readily estimated in the crude oxalates from monazite.

As acid solutions of ceric salts remained unchanged for a long time, but yet are powerful oxidising agents, they can be used where permanganate is not applicable, as, for example, in the estimation of oxalic acid in the oxalochlorides, the excess of the reagent being determined by means of hydrogen peroxide solution. The solution can be prepared from ordinary commercial cerium compounds, since the presence of the other monazite metals has no influence on the results.

C. H. B.

**Estimation of Manganese by Means of Potassium Permanganate.** By FREDERIC W. DAW (*Chem. News*, 1899, 79, 25, 58, 104—105; HARRY BREARLEY, *ibid.*, 47, 83—84).—Daw regards the presence of organic matter, the reckless use of zinc oxide in large quantities, and the standardising of the permanganate with iron instead of manganese, as sources of error in the estimation of manganese by means of permanganate, and describes a method in which these errors are eliminated. Incidentally, in the analysis of the standard ferromanganese, he ignites the trimanganic tetroxide over a blow-pipe in a platinum crucible, and in answer to remarks by Brearley on the probable effect of the permeability of heated platinum to gases on the result, he quotes some very concordant results obtained over the blow-pipe, as compared with unsatisfactory ones obtained in an underheated muffle. If iron is used to standardise the permanganate, a figure is obtained which gives low results when working on manganese, and is attributed to want of knowledge of the actual reaction that does take place, although Brearley is inclined to

credit the carbon in the iron as having some influence ; this, however, Daw does not admit. D. A. L.

**Separation of Iron from Zirconium and Allied Metals.** By J. MERRITT MATTHEWS (*J. Amer. Chem. Soc.*, 1898, 20, 846—858).—The author gives a *résumé* of the methods which have been suggested for the separation of iron and zirconium, and then describes a method based on the solubility of ferric chloride and the insolubility of zirconium oxychloride in dry ether. The aqueous solution is evaporated to dryness on a water-bath, and when cold the residue is treated with dry ether and saturated with hydrogen chloride, in order to dissolve the iron ; the solution is filtered, the residue washed with dry ether, then dissolved in water, and the zirconium precipitated as hydroxide. The ethereal solution is evaporated to dryness and the iron precipitated as hydroxide. A similar method may be adopted for separating iron from thorium, cerium, titanium, &c. The method is similar to that described by Gooch and Havens (*Abstr.*, 1897, ii, 232) for the separation of aluminium from iron. J. J. S.

**Some Characteristic Reactions of Nickel and Cobalt.** By G. PAPASOGLI (*L'Orosi*, 1898, 21, 265—266).—If a slight excess of a solution containing 2 per cent. of sodium hydroxide and 10 per cent. of cane sugar is added to a solution of a cobalt salt, a clear blue-violet coloured liquid is obtained, whilst nickel, if present, is precipitated as the greenish-white hydroxide. In presence of much cobalt, a little of the nickel remains in solution and the liquid is opalescent. If, on the other hand, the nickel is in large excess, part of the cobalt is precipitated along with it, and the blue-violet coloration is diminished in intensity, or may not be produced at all. Nevertheless, cobalt may be detected in the solution by filtering the liquid and adding a few drops of sodium amylic dithiocarbonate solution (obtained by adding a mixture of equal volumes of amylic alcohol and carbon bisulphide to an equal volume of 50 per cent. soda), when a yellowish-green coloration is produced, which changes to maroon on adding yellow ammonium sulphide. The presence of nickel is confirmed by the blood-red coloration obtained when the precipitate remaining on the filter is dissolved in ammonia and sodium amylic dithiocarbonate is added to the solution. N. L.

**Occurrence of Chromic Oxide in Algerian Phosphates.** By GEORG SCHÜLER (*Zeit. angew. Chem.*, 1898, 1101—1103).—Algerian phosphates and the superphosphates made from them may be distinguished from other products by the small but distinct traces of chromium they contain. As a solution of chromic oxide in phosphoric acid is intensely green, the superphosphate made from Algerian phosphate is often distinctly green. Some samples of the raw material contained as much as 0.057 per cent. of chromic oxide.

The presence of chromium is easily proved by adding to the hydrochloric acid solution of the phosphate a large excess of ammonia ; if a slight excess of acetic acid is now added to the greenish liquid, and the whole boiled, green chromic phosphate is precipitated, which may

be converted into sodium chromate by adding sodium dioxide and boiling. The estimation is made in the usual way by boiling the slightly acid solution of the phosphate with sodium dioxide, and destroying the excess by continued boiling; the solution is then acidified and titrated.

L. DE K.

**Analysis of Molybdenum Compounds.** By HARRY BREARLEY (*Chem. News*, 1899, 79, 2—4, 14—15. Compare this vol., ii, 129).—To obviate the interference of sulphuric acid in the estimation of molybdenum as lead molybdate, the mixture containing molybdic and sulphuric acids is heated to boiling, and into it is poured excess of a hot solution of lead acetate to which 30 c.c. of strong ammonium acetate has been added. Barium, if present in the molybdic solution, may be safely removed as sulphate after slightly acidifying with hydrochloric acid; but as strontium and calcium molybdates are more soluble than the barium salt, they may be disposed of by adding to the boiling molybdic solution a slight excess of hydrochloric acid, then acetic acid, lead acetate, and finally ammonium acetate, when the boiling is stopped and filtration proceeded with. This treatment is also serviceable in the presence of arsenic, cadmium, aluminium, and chromium, and in the estimation of molybdenum in alkali molybdates. Silica may be eliminated by boiling with hydrochloric acid and filtering, with or without a preliminary evaporation to dryness and ignition. The separation of iron and molybdenum presents special difficulties, precipitation as basic acetate being quite useless for the purpose, as molybdenum and iron are precipitated together; in fact, it is probable the alkali molybdates may serve for the separation of iron from other members of its group.

The separation of chromium from molybdenum by means of ammonia or soda is unsatisfactory; in the latter case, some sodium chromate is always formed, and is precipitated as lead chromate with the molybdenum, and although this factor decreases with the excess of soda used, it cannot be entirely eliminated. In the most satisfactory mode of procedure, excess of sodium hydroxide is added to the boiling hot, nearly neutral, solution of molybdenum and chromium, or, if the latter largely preponderates, the solution is added to the soda with constant shaking. After boiling for 10 minutes, the molybdenum is precipitated in a filtered aliquot part of the mixture; the lead molybdate, probably coloured yellow by chromate, is redissolved in hydrochloric acid, treated with dilute soda until the precipitate is just redissolved, and after boiling, filtering, and treating with lead acetate, the molybdenum is again precipitated; the best result is obtained with an excess of 10 c.c. of 2*N* soda. Reduction of the chromic acid is of no use for this separation. If chromic chloride is present, lead acetate is added, the cold solution slightly acidified with hydrochloric acid, and then ammonium acetate until the precipitate redissolves. On boiling, a precipitate forms, and in 10 or 15 minutes the whole of the molybdenum separates; this precipitate is ignited, boiled with hydrochloric acid, and the lead molybdate precipitated and redissolved in the manner already described; this is a most expeditious method of analysing a chrome-molybdenum.

In the presence of phosphoric acid, the formation of phosphates and phosphomolybdates causes trouble, which cannot be overcome by the use of glycerol, although lead molybdate may be accurately precipitated in the presence of that substance; but the following treatment rigorously followed overcomes the difficulty. Hydrochloric acid is added to the solution containing the molybdic and phosphoric salts in quantity sufficient to retain in solution the lead salts which are formed when enough lead acetate is added to combine with all the molybdenum and phosphorus. The heated solution is poured into, and well shaken with, a hot solution containing 10 to 15 grams of ammonium chloride, and sufficient ammonium acetate to react with the free hydrochloric acid; the whole is digested a few minutes and filtered; the filtrate should be tested for lead and the precipitate ignited. If it contains phosphorus, it is redissolved in hydrochloric acid, and the treatment with ammonium acetate and chloride repeated. To test for phosphorus, the precipitate is dissolved in hydrochloric acid, and dilute ammonia added very carefully so that any phosphomolybdate will appear before the lead molybdate; or excess of ammonia may be added at once, and the precipitate carefully redissolved in nitric acid; moreover, if only 1 or 2 per cent. of lead phosphate is present, an approximately accurate result may be obtained by completing the precipitation of the phosphomolybdate, weighing it, and allowing for it.

*Estimation of Phosphorus.*—It is suggested that the above method might advantageously be applied to the gravimetric estimation of the molybdenum in ammonium phosphomolybdate, and so replace the usual volumetric practice.

In the estimation of lead as molybdate, Chatard (*Chem. News*, 1871, 24, 175) found that excess of the precipitant caused cloudiness; this may be overcome by using ammonium chloride before or with the alkali molybdate. As regards the precipitation of lead, excess of molybdate added to a lead solution containing sufficient hydrochloric acid to prevent precipitation in the cold, causes a precipitate to form on warming, whilst with excess of lead acetate the reverse is the case. When in the method of treating a mixture of hydrochloric acid, acetic acid, lead acetate, and ammonium acetate with an excess of molybdate, the lead molybdate is contaminated with molybdic acid, it may be redissolved in hydrochloric acid and reprecipitated with ammonium acetate, but without any further addition either of ammonium molybdate or lead acetate; or it may be reprecipitated with an excess of lead acetate, weighed again, the difference between the first and second weighings calculated as molybdic anhydride, and this deducted from the first weight.

D. A. L.

*Estimation of Tungsten.* By HARRY BREARLEY (*Chem. News*, 1899, 79, 64—66).—The precipitate formed by lead acetate in acid solutions of tungstates always consists of lead tungstate mixed with a variable quantity of tungstic acid; in alkaline solutions, and in neutral solutions (owing to the difficulty of maintaining neutrality) there is an admixture of lead oxide. Therefore the following method was devised to ensure the formation of lead tungstate without

contamination. Two or three grams of ammonium nitrate and a faint excess of nitric acid are added to the alkaline tungstate, which is boiled for a few minutes, and then treated with a small excess of ammonia and an excess of lead acetate. Lead tungstate mixed with a small quantity of basic lead compound is formed, but the latter is redissolved by a few minutes brisk boiling, and the former can be ignited and weighed for the estimation of the tungsten.

A method of analysing the lead tungstate which may serve, moreover, for the separation of molybdenum and tungsten is as follows. Lead tungstate is boiled with a large excess of concentrated hydrochloric acid until the clear solution becomes opalescent, but not yellow; it is then diluted with water to the extent of four or five times the volume of the acid used, when subsequent boiling for a few minutes brings down all the tungsten as trioxide. Nitric acid also precipitates the trioxide, but it then adheres to the glass, which, in the present instance, is not the case. The trioxide is washed with very dilute hydrochloric acid, filtered, ignited, &c. The lead may be determined in the filtrate by neutralising with ammonia, acidifying with acetic acid, and precipitating with a clear solution of sodium or ammonium molybdate as described in the preceding abstract. D. A. L.

**Reaction of the Arsenic-Tin Group.** By J. DUCOMMUN (*Chem. Centr.*, 1898, ii, 1218—1219; from *Schweiz. Wochschr. Pharm.*, 36, 433—434).—If a little strong formaldehyde is added to ammonium sulphide, an abundant, white precipitate is formed, which redissolves on adding a little strong sulphuric acid; very dilute ammonium sulphide gives no precipitate at all. If the liquid contains arsenious anhydride, sulphuric acid yields a white precipitate insoluble in excess; if arsenic acid is expected, the solution should be first boiled before decolorising with formaldehyde. Antimony gives a clear orange-red, tin a white, gold a yellowish-white, and platinum a brownish-red precipitate. This reaction may be utilised in qualitative analysis as follows. The acid liquid is nearly neutralised with ammonia, mixed with excess of ammonium sulphide, and boiled so as to dissolve the platinum sulphide and reduce any arsenic acid. A part of the filtrate is then largely diluted, and mixed with formaldehyde and sulphuric acid; if no precipitate is formed, the metals of the arsenic-tin group are absent. If a precipitate forms, the rest of the liquid is treated in the usual way; if not sufficiently diluted, a cloudiness will form, due to traces of copper, lead, or mercury, which are not quite so insoluble in ammonium sulphide as is generally believed.

The precipitate insoluble in ammonium sulphide may be boiled with dilute hydrochloric acid to dissolve the metals of the iron group.

L. DE K.

**[Estimation of Iridium in Commercial Platinum.]** By PAUL BERGSÖE (*Zeit. anorg. Chem.*, 1899, 19, 318—326).—See this vol., i, 321.

**Toxicological Detection of Acetylene.** By DIOSCORIDE VITALI (*L'Orosi*, 1898, 21, 217—224).—In cases of poisoning by acetylene, the gas is to be found chiefly in the blood and lungs, and the method recommended for its detection is based on the solubility of acetylene



in acetone, and on the fact that it is simply dissolved in the blood and not chemically combined with it. Some of the blood is mixed with 5—8 per cent. of its volume of acetone, the liquid distilled at 55—60°, and the usual tests applied to the distillate. If the blood has undergone putrefaction, some ferrous sulphate should be added to the liquid before distillation, in order to decompose ammonium sulphide and carbonate. The air remaining in the lungs may be examined by connecting the trachea with an aspirator and drawing the air through a washing apparatus containing a little acetone. The acetylene prepared from commercial calcium carbide is frequently contaminated with compounds of sulphur and phosphorus; these may be detected by gently warming the acetone solution with chlorine water, and subsequently applying the usual tests for sulphuric and phosphoric acids.

It is observed that acetylene has considerable antiseptic properties, since a solution of blood, saturated with acetylene, showed no signs of putrefaction after being kept for three months. N. L.

**Analysis of Wine and Vinegar.** By L. ERCKMANN (*Chem. Zeit.*, 1898, 22, 673).—A number of diseased wines have been analysed. It sometimes happens that fermentation stops suddenly, and the liquid then contains from 0.2 to 2 per cent. of sugar and about 2 per cent. of volatile acids; the flavour is then like that of vinegar, but frequently there is also a disgusting taste. When evaporated to dryness, the residue from such wines frequently contains a number of needle-shaped crystals of mannitol.

The growers often attempt to render such wine saleable by neutralising the acid with lime, but as the fixed acids are neutralised before the acetic acid, the wine will contain calcium malate, which causes a crust to be formed should the wine dry on the outside of the bottle. If the greater portion of the acetic acid has also been neutralised, the extract will contain a large excess of organic calcium salts, and such a residue cannot be properly dried, even if it is moistened with water and again evaporated before placing it in the water oven.

The alcohol contained in wines or vinegars may be estimated by distillation, but the acid must first be neutralised with soda; it is, therefore, best to use the portion in which the acidity has been estimated with standard soda.

The extract of vinegar is best analysed by the process given for wine. In determining the ash of vinegar, it is advisable to cover the residue with filter paper free from ash, so as to prevent loss by the decrepitation which always occurs when heating. L. DE K.

**Estimation of Pentosans.** By W. L. A. WARNIER (*Rec. Trav. Chim.*, 1898, 17, 377—383).—The author has made estimations of the amounts of furfuraldehyde obtained by distilling hexoses, dextrins, pentosans, and crude vegetable products with 12 per cent. hydrochloric acid, using the method recommended by Counciler (*Abstr.*, 1895, ii, 144). He concludes that hexoses, under the prescribed conditions, yield only very small quantities of furfuraldehyde. Two explanations of this fact are possible, namely, that the furfuraldehyde is produced by a slow carbonisation, which is, to some extent, restrained by the tem-

perature of the liquid, or that its formation is due to the presence of a small quantity of impurity in the sugar, which is not removed by treatment with absolute alcohol; the gradual diminution of furfuraldehyde, with increased purity of the hexose, appears to support the latter view. Further, the modern method of estimating pentosans has certain faults due to difficulty of manipulation, and also to the fact that the pentosans in the products which yield the furfuraldehyde have not been obtained in a pure state.

A. L.

**A Colour Reaction of Wood.** By ARNALDO PIUTTI (*Gazzetta*, 1898, 28, ii, 168—170).—Orthobromophenetidine hydrochloride imparts a deep yellow colour to wood, but not to cellulose, the ordinary textile fibres, chitin, or chitin. This reagent can, therefore, be used for determining approximately the quantity of wood-pulp added to paper, as the yellow tint is still given by wood from which all extractable matter has been removed. The hydrochlorides of other bases, such as orthobromanisidine, ortho- and para-amidophenol, paranisidine, parphenetidine, act similarly. The coloration is probably due to an aldehydic reaction of the wood with the amido-group.

T. H. P.

**The Ferric Chloride Test for Phenol.** By FRANZ PETERS (*Zeit. angew. Chem.*, 1898, 1078).—It is well known that the violet-blue colour which aqueous solutions of phenol give with ferric chloride is not developed in alcoholic solutions. The author has made experiments in order to ascertain how much alcohol is required to render the test nugatory. He finds that a 4 per cent. aqueous solution of phenol may be mixed with 3.19 per cent. of absolute alcohol by volume (or with 2.53 per cent. by weight), without interfering with the test; the reaction is indistinct when the quantities are increased to 3.44 (or 2.73) per cent. If the solution contains more alcohol than this, a blue colour is not produced.

L. DE K.

**Arachidic Acid in Rape and Mustard Oils.** By LEONARD ARCHBUTT (*J. Soc. Chem. Ind.*, 1898, 17, 1009).—According to Ponzio (*Abstr.*, 1894, i, 115), rape oil contains about 0.4 per cent. of arachidic acid, but the author finds that genuine rape-oil may contain as much as 1.43 of so-called arachidic acid (m. p. 70—72°), which is really a mixture of arachidic and lignoceric acids, although, in certain samples the amount of these acids present is practically *nil*. The same mixture of acids is met with in mustard oil; it therefore follows that the finding of arachidic acid in olive oil is not conclusive proof of the presence of earth-nut oil, unless it has been proved that rape and mustard oils are absent.

J. J. S.

**Estimation of Tartaric Acid.** By PAUL KULISCH, P. KOHLMANN, and MAX HÖPPNER (*Zeit. angew. Chem.*, 1898, 1143—1146, and 1899, 6—9).—A criticism on the process used by German Government analysts for estimating the amount of tartaric acid in the various forms in which it occurs in wine. To perform the analysis, it is necessary to estimate the total tartaric acid, the alkalinity of the aqueous solution of the ash, and the alkalinity of the ash itself.

New formulæ are given to facilitate the calculation, and slight

sources of error, such as the presence of other organic acids, are indicated. The correct estimation of the alkalinity of that portion of the ash which is soluble in water is practically impossible, as the so-called insoluble ash is not perfectly insoluble and the washings are still alkaline; it would, therefore, be advisable for analysts to agree to wash it with a definite volume of water.

In estimating the total tartaric acid by the Halenke-Möslinger process, which consists in converting the acid into potassium hydrogen tartrate by means of potassium acetate, the official instruction is to add 2 or 3 drops of a 20 per cent. solution of this salt; the authors state that in some cases this is insufficient.

L. DE K.

**Detection of Salicylic Acid in Wine, Beer, &c.** By A. ABRAHAM (*J. Pharm.*, 1898, [vi], 8, 410—411; from *J. Pharm. Liège*, July, 1898, 173).—For the detection of salicylic acid in beer, Jorissen's method is recommended, Rose's not being applicable. To detect the acid in wine, 200 c.c. is extracted with a mixture of ether and light petroleum, and the residue left on evaporating the ethereal extract is distilled with a mixture of 15 c.c. of distilled water and 5 c.c. of syrupy phosphoric acid; the salicylic acid is easily detected in the distillate by the usual tests (bromine water, ferric chloride, &c.). This method admits of the detection of 0.08 gram of salicylic acid per litre, even in the presence of 10 per cent. of tannin.

H. R. LE S.

**Distinctive Reactions of Tannin and Gallic Acid.** By GIUSTINIANO TODESCHINI (*L'Orosi*, 1898, 21, 328—330).—According to David, when potash and barium chloride solution are added to a solution of tannin, a red precipitate is produced, the colour of which gradually increases in intensity, whilst with gallic acid, under similar conditions, a blue precipitate is obtained. The author confirms the reaction in the case of gallic acid, but finds that the results obtained with tannin vary with the dilution. Thus, with a 1 per cent. solution of tannin a green precipitate, changing to greenish-blue, is formed, whilst with a 0.1 per cent. solution, and especially in the presence of much potash, a somewhat reddish-yellow precipitate is obtained, which at first increases and then diminishes in intensity. Potash alone gives with tannin and with gallic acid a greenish coloration, becoming of an intense red on agitation with air, and it seems probable that the red colour observed by David with tannin is due to this reaction, which is more apparent with tannin than with gallic acid, since the precipitate given by the former with potash and barium chloride is less abundant and not so intensely coloured.

A list of the reactions of gallic acid and tannin is given. N. L.

**Analytical Notes [Tannin: Iron in Water: Zinc Iodide Starch Solution].** By ANTON SEYDA (*Chem. Zeit.*, 1898, 22, 1085—1086).—*A Delicate Test for Tannin.*—The author has noticed that if gold chloride is added to a very dilute solution of tannin, a clear, purple coloured liquid is obtained; this test is so sensitive that it gives a reddish colour with claret which has been so largely diluted

with water as to be practically colourless. In extremely dilute solutions, it will take about half an hour before the colour is fully developed, and this is perhaps the reason that the extreme delicacy of the reaction has not been previously noticed. Its principal use is to detect tannin in highly coloured extracts; the test may also be useful in microscopy.

*Colorimetric Estimation of Iron in Water.*—The process recommended is practically the same as that devised by Lunge (Abstr., 1896, ii, 392). The author, however, recommends the destruction of any organic matter by evaporating the water to dryness and igniting the residue, which is then fused with a little sodium hydroxide to render the iron more soluble.

*Preparation of Zinc Iodide-Starch Solution.* Two to three grams of potato starch is mixed in a mortar with 50—100 c.c. of water, and after an hour the emulsion is heated in a pressure flask in an oil bath at 130° for 2 to 4 hours; when cold, the liquid is rinsed into a litre flask with about 750 c.c. of hot water, and after 24 hours filtered through a quick filter. A solution of 20 grams of zinc chloride and 2 grams of zinc iodide is then added, and should a bluish colour be noticed this is removed by means of a very dilute solution of sodium thiosulphate. The mixture, diluted to one litre, is left for 24 hours before being filtered. This solution will keep indefinitely if a bottle of brown glass be used.

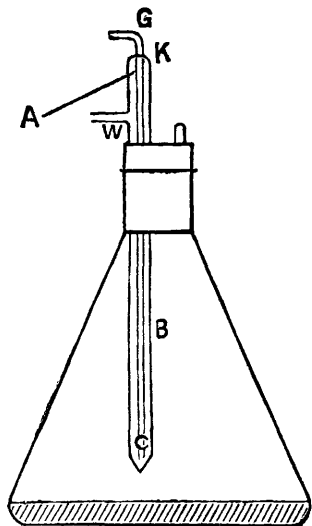
L. DE K.

*Reactions of Bile Acids and their Detection in Urine.* By DIOSCORIDE VITALI (*L'Orosi*, 1898, 21, 397—407).—Two new reactions of glycocholic and taurocholic acids are described. If about 0.5 c.c. of concentrated sulphuric acid is added to a fragment of the bile acids, or to the cooled residue obtained by evaporating their solution to dryness, a yellow coloration is produced which, on warming, becomes orange-red and then blood-red. On still further heating and adding more sulphuric acid, the liquid acquires a beautiful green fluorescence which is destroyed on adding water; this reaction, which is also given by cholic acid and by cholesterol, is obtained with 0.00001 gram of bile acids. In the presence of other organic substances giving a brown colour with sulphuric acid, the yellow and red colorations described may be obscured, but the green fluorescence may still be obtained if a large volume of sulphuric acid is employed. In the second reaction, after adding sulphuric acid as before, a few drops of weak chlorine water are cautiously added, when green striae, changing to blue, violet, and red, are seen at the junction of the two liquids, and on adding more sulphuric acid, the green fluorescence is produced.

As neither of the above reactions can be directly applied to urine, the bile acids must be first extracted, either by Hoppe-Seyler's process or by one of four methods, described in detail in the paper, based on the dissolution of the acids in amylic alcohol or in a mixture of alcohol and chloroform, or on their precipitation as the quinine salts or in combination with albumin. If bile pigments are present, they must be removed by treatment with freshly prepared lead sulphide according to the method previously described by the author.

N. L.

**Apparatus for the Saponification of Fats, &c.** By J. G. ANNAN (*Chem. News*, 1899, 79, 51).—The weighed fat and alcoholic potash are charged into an Erlenmeyer flask and a doubly bored cork is inserted, in one hole of which the condensing arrangement shown in the cut is fixed and connected at W with a water supply; the flask is gently heated until the air is displaced, when a glass plug is put in the other hole. A current of cold water is now caused to circulate in the tube B, entering at W, and escaping at G, and the liquid in the flask may be boiled vigorously without any further attention until saponification is complete. The tube B is 5 inches long, and 3/8-inch bore, the tube C 1/8-inch bore. D. A. L.



**Detection of Phytosterol and Cholesterol in Fats.** By HANS KREIS and OTTO WOLF (*Chem. Zeit.*, 1898, ii, 805—806).—Fifty grams of the sample is saponified by boiling with 125 c.c. of 95 per cent. alcohol and 25 c.c. of 40 per cent. aqueous soda; when the fat has dissolved, the solution is evaporated in a spacious porcelain dish until the bulk of the alcohol has been driven off. The soap is then dissolved in 500 c.c. of boiling water, transferred to a 2-litre flask, nearly neutralised with hydrochloric acid, using phenolphthalein as indicator, and 100 c.c. of a 10 per cent. solution of calcium chloride is added at once, shaking the mixture well to facilitate separation of the lime-soap. The precipitate, which is collected on a cloth and pressed dry, finally between blotting paper, contains all the cholesterol or phytosterol. The powdered lime-soap is boiled for an hour with 100 c.c. of alcohol, filtered when cold, and the filtrate mixed with 3 c.c. of aqueous soda and evaporated to dryness to saponify any fat which may have escaped decomposition. The residue is powdered and extracted in a closed flask with 50 c.c. of ether for an hour, shaking frequently, the ether evaporated, and the residue recrystallised from a very small quantity of boiling alcohol; the phytosterol or cholesterol is then obtained in a pure and white condition.

The authors have successfully applied this process to butter, lard, and cotton-seed oil. Quantitative experiments will be reserved for a future paper.

L. DE K.

**Toxicological Processes for Detecting Alkaloids.** By ANTON SEYDA (*Chem. Centr.*, 1898, 2, 1288—1289; from *Zeit. öffentl. Chem.*, 4, 699—705; 721—747; 762—769).—It is needful to examine the contents and membranes of the bladder, as these often contain the poison when the other organs do not. The investigation is rendered more troublesome when medicines have been administered, such as prepara-

tions of colombo, rhatany, mercury, &c. If the organs are in an advanced state of decomposition, ptomaines are formed which interfere with the tests for opium alkaloids and strychnine. Meconic acid and meconine cannot be always detected, as these are decomposed both during life and after death.

In bodies which are likely to contain ptomaines, the opium or *Strychnos* alkaloids are best searched for by the gypsum method recommended by Hilger and Küster; Kippenberger's iodine process for the purification of the crude alkaloids extracted by chloroform was also found to be very satisfactory. It is desirable that new solvents for the extraction of the alkaloids should be tried.

L. DE K.

**Piutti's Reagent for Alkaloids (Iodised Parethoxyphenylsuccinimide).** By GUIDO SIMONCELLI (*Gazzetta*, 1898, 28, ii, 171—177).—By comparative titrations of quinine hydrogen sulphate with an acetic acid solution of Piutti's reagent and one of equivalent strength of iodine and potassium iodide, the author finds that the same volume of either solution will completely precipitate the alkaloid, and that in the case of the former the parethoxyphenylsuccinimide is not precipitated, but remains undecomposed in solution in the acetic acid; the precipitates obtained in the two cases are identical.

Using solutions of quinine and brucine, the relative sensitiveness to these alkaloids of Piutti's reagent, of an equivalent solution of iodine in potassium iodide, of Bouchardat's and of Selmi's reagents was determined; the results show that there is little difference between Piutti's reagent and the iodine solution, and that both these are more sensitive than Bouchardat's or Selmi's reagent.

T. H. P.

**Piutti's Reagent for Alkaloids.** By NINO SCARPITTI (*Gazzetta*, 1898, 28, ii, 177—189. See preceding abstract).—The author has extended the experiments made by Simoncelli to the following alkaloids:—Atropine, quinidine, cinchonidine, cinchonine, cocaine, codeine, coniine, daturine, hydrastine, morphine, narcotine, nicotine, papaverine, sparteine, strychnine, and veratrine. His results show that Piutti's reagent is much more sensitive than either Bouchardat's or Selmi's, or than a solution of iodine in potassium iodide. Voluminous tables accompany the paper.

T. H. P.

**Detection of Quinine in Urine by Means of Picric Acid.** By ANASTASIOS CHRISTOMANOS (*Chem. Centr.*, 1898, ii, 1284—1285; from *Berl. klin. Wochschr.*, 35, 976).—Quinine may be detected in urine by the dense, yellowish-white precipitate given by picric acid, which is quite distinct in appearance from that due to uric acid or creatinine. No precipitate is yielded in the urine after partaking of caffeine, antipyrine, phenacetin, salol, or sodium salicylate, but albumin, unless there is only a mere trace, interferes with the test, as it is also precipitated by picric acid. On attempting to remove the albumin by boiling, the quinine is also precipitated.

L. DE K.

## General and Physical Chemistry.

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**Changes of Rotation of Active Electrolytes in Dilute Solutions.** By EBERHARD RIMBACH (*Zeit. physikal. Chem.*, 1899, 28, 251—256).—The absolute values for the dissociation of rubidium tartrate obtained from the rotation do not agree with the conductivity determinations, although the relative values are in fair accord, and it is considered probable that the value for infinite dilution obtained by extrapolation was inaccurate (*Abstr.*, 1895, ii, 301). In order to further test the influence of dilution and dissociation on rotation, the latter constant was determined up to very high dilutions for the slightly dissociated mandelic acid and the more highly dissociated sodium salt, and the values compared with those obtained from the linear formula of Lewkowsitch. In the case of the sodium salt, the values agree, even with a concentration of somewhat below 1 per cent., but differ to the extent of 3 per cent. in a 0.05 per cent. solution, whilst, for the acid itself, the difference between the found and calculated values becomes apparent at a concentration of 3 per cent., and rapidly increases with further dilution, so that extrapolation for the value at infinite dilution can only be applied with strong electrolytes.

L. M. J.

**Dissociation Spectra of Fused Sulphates, Sulphides, Phosphates, and Salts containing both Sulphur and Phosphorus.** By ARNAUD DE GRAMONT (*Bull. Soc. Chim.*, 1898, [iii], 19, 54—57, 57—58, and 58—59).—The spark spectra of alkali sulphates and sulphides exhibit the chief lines of Salet's spark spectrum of sulphur; the following groups of lines can also be observed:  $S\phi$ ,  $\lambda = 6416.5, 6402.5, 6390$ , and  $S\psi$ ,  $\lambda = 6320.0, 6309.5$ , and  $6291$ . The spark spectra of fused alkali phosphates and of metals containing phosphorus exhibit the principal lines of the non-metal; the presence of phosphorus in samples of cast iron can be readily detected by the lines 6043, 6035, and 6026 of the well-defined triplet Pa, although these become invisible when less than 0.1 per cent. is present. The spectra of thiophosphates (*Friedel, Abstr.*, 1895, ii, 13) exhibit the principal lines of both sulphur and phosphorus, those of the latter being very strongly defined; the lines of sulphur only become visible when the condenser employed has a surface area greater than 25 square decimetres. Detailed measurements are given in the papers; it appears that the spark spectrum affords a delicate method of detecting the elements dealt with, in solid compounds, even when these are almost non-conducting.

W. A. D.

**Osmotic Theory of the Galvanic Cell.** By WALTHER NERNST and EMIL BOSE (*Zeit. Elektrochem.*, 1898, 5, 233—235).—According to the osmotic theory of the galvanic cell, the potential difference between a metal and a solution is  $E = RT/n \log C/c$ . The electrolytic solution tension of the metal,  $C$ , and the number of electric charges with which it passes into the ionic state,  $n$ , depend on the nature of

the metal alone. By changing the concentration,  $c$ , of the metallic ions in the solution in any way, the potential difference,  $E$ , must also be changed. To test this, a mercury electrode covered with mercurous sulphate and a slowly-dropping mercury electrode, are placed in glass tubes containing normal sulphuric acid, and connected by a long, narrow, horizontal tube. The tube containing the dropping electrode contains, in addition, two platinum electrodes, by means of which any traces of metal may be removed from the solution in contact with the dropping mercury by electrolysis. The potential difference between the two mercury electrodes must be measured by an electrometer, the dropping electrode being polarised excessively readily. The highest potential difference observed was 0.443 volt. With silver electrodes in 0.01 normal hydrochloric acid, the acid surrounding one of them being saturated with silver chloride, a maximum potential difference of 0.423 volt was obtained. The results are thus in agreement with the theory. T. E.

**Modifications of Common Galvanic Cells.** By EMIL PETERSEN (*Zeit. Elektrochem.*, 1898, 5, 261—265).—When the sulphuric acid in the Bunsen cell is replaced by a saturated solution of common salt, the E.M.F. is not altered, and the internal resistance is hardly changed; it is slightly increased if a solution of 4 parts of sodium nitrate in 5 parts of water is used. The nitric acid may be replaced by other oxidising agents, but the constancy of the cell suffers. A cell arranged as follows:  $\text{Zn} \mid \text{NaCl solution (1:5), FeCl}_3 \cdot 6\text{H}_2\text{O solution (2:1)} \mid \text{carbon}$ , has an E.M.F. of 1.72 volts. It will give a current of not more than 1 ampère for hours at constant E.M.F. The principal reaction is  $\text{Zn} + 2\text{FeCl}_3 = \text{ZnCl}_2 + 2\text{FeCl}_2$ ; the secondary reaction,  $3\text{Zn} + 2\text{FeCl}_3 + 6\text{H}_2\text{O} = 3\text{ZnCl}_2 + 2\text{Fe(OH)}_3 + 3\text{H}_2$ , also occurs. When the ferric chloride is entirely reduced, the E.M.F. sinks to about 0.5 volt, and metallic iron is deposited on the carbon. The cell is now a very constant one of the Daniell type. If the porous cell is left out, the combination  $\text{Zn} \mid \text{FeCl}_3 \text{ solution} \mid \text{C}$  gives 1.6 volts;  $\text{Fe} \mid \text{FeCl}_3 \text{ solution} \mid \text{C}$  gives 0.9 volt. Potassium ferricyanide is an efficient substitute for the nitric acid in the Bunsen cell so long as no large amount of ferrocyanide is present. The E.M.F. diminishes gradually from 1.438 volts with pure ferricyanide to 1.105 volts with pure ferrocyanide. A convenient form of Daniell cell, in which magnesium chloride is used in place of zinc sulphate, is also briefly described. T. E.

**Potential Difference between Amalgams and Solutions.** By AUGUST SCHOELLER (*Zeit. Elektrochem.*, 1898, 5, 259—261).—According to Nernst's theory, the difference of potential,  $E$ , between amalgams of an alkali or alkaline-earth metal of different concentrations,  $C$  and  $C_1$ , in contact with the same solution, is given by the formula  $E = 0.000198T/n \log C_1/C$ , where  $T$  is the absolute temperature and  $n$  the number of electrical charges carried by an ion. The author prepares the amalgams by electrolysis of saturated solutions of baryta and of caustic soda. The concentration of the amalgam and the potential difference between it and the solution are then measured, and the results compared with those required by the theory, a very



close agreement being found. It follows, therefore, that the solution tension of a metal dissolved in mercury is proportional to its concentration. The saturated solution of barium in mercury at  $10^{\circ}$  contains about 0.23 per cent. of barium. T. E.

**Contact Potential between Metals and Melted Salts, and the Dissociation of Melted Salts.** By CLARENCE MCCHEYNE GORDON (*Zeit. physikal. Chem.*, 1899, 28, 302—312).—The E.M.F. was determined for cells consisting of silver electrodes immersed in two molten mixtures of silver nitrate in potassium and sodium nitrates, of different concentration as regards the silver nitrate. Temperatures of  $232$ — $236^{\circ}$  were obtained by a quinoline bath, and of  $298^{\circ}$  by a diphenylamine bath, and the concentrations of the solutions examined were 1/0.1, 10/1, 50/10, and 100/50. The results for the two lower concentrations agreed completely with those calculated by Nernst's formula, and even for the high concentrations the difference only reached about 12 per cent. The dilute solutions are, therefore, almost completely dissociated, whilst from the values for the actual E.M.F. the values for dissociation in the 50 per cent. and 100 per cent. solutions are calculated as 0.69 and 0.58 respectively. This very high dissociation serves to explain the great conductivity of pure melted salts. L. M. J.

**Chemical Proof of Concentration Change with Drop-electrodes.** By WILHELM PALMAER (*Zeit. physikal. Chem.*, 1899, 28, 257—279).—According to Nernst's theory, the concentration of the solution in the upper portion of a mercury dropping electrode should decrease whilst that of the lower liquid should increase, and experiments were made by chemical methods with the view of proving that these changes occur. The apparatus employed is described, the most noticeable feature being a new form of dropping tube, in which the mercury drops through about 100 fine, vertical grooves etched on the surface of a glass plug, and by the use of which measurable results are rapidly attained. The solution employed was N/0.0005 mercurous nitrate, which, however, contained a slight excess of nitric acid. In 5 minutes, the mercury concentration in the upper liquid had decreased in the ratio 0.42:1, and had increased in the lower liquid in the ratio 1.76:1, the similar ratios for the nitric acid being 0.87 and 1.11. The mercury was estimated by a colorimetric hydrogen sulphide method, and the nitrates by indigo solution. The results are in accord with Nernst's theory, but in no way contradictory to other theories of electrocapillary phenomena (compare *Abstr.*, 1898, ii, 276). L. M. J.

**Sources of Error in the Silver Voltameter.** By K. KAHLE (*Ann. Phys. Chem.*, 1899, [ii], 67, 1—36).—The author investigates the causes of the slight differences in the weight of silver deposited in two voltmeters coupled up in series, and shows that, when both are treated in a similar manner, the difference is only about 1 part in 10,000. If the precipitate is washed with warm water, a loss in weight of about 1/4000 occurs, and it is found that a slightly smaller weight of silver is deposited on platinum than on a surface which is

already coated with silver. If the same solution of silver nitrate is used in a large number of experiments, the weight of precipitated silver is about  $1/1000$  greater than when a fresh solution is used, and the precipitate separates in larger crystals; under these conditions, the solution becomes acid, and a similar increase in the weight of silver deposited is produced by the addition of acid to a freshly prepared solution, whilst the abnormal results disappear if the solution is shaken up with silver oxide. If a considerable quantity of acid is present (20 milligrams of  $\text{HNO}_3$ : 1 gram  $\text{AgNO}_3$ ), a brownish-violet precipitate is formed, which, when heated with water, becomes yellow at  $30^\circ$  and disappears at  $40^\circ$ ; at the same time, the anode becomes brown instead of grey. This violet precipitate only forms in the part of the voltmeter below the anode, and if the anode is placed in a separate vessel and connected by a syphon to the dish which forms the cathode, no such precipitate is produced; the formation of a coloured precipitate can also be prevented by shaking the solution with molecular silver. When silver oxide is added to the nitrate solution, the weight of silver deposited is  $1/2000$  greater than in a neutral solution.

In all these experiments, the current was adjusted so that no current passed through a Clark cell in parallel with a 4-ohm coil; the mean weight of silver deposited in 40 minutes was 0.9723 gram, and taking the electrochemical equivalent of silver as 1.118 mg. per coulomb, the E.M.F. of the Clark cell is found to be 1.4494 volts at  $0^\circ$ , and therefore 1.4330 volts at  $15^\circ$ . An indirect determination gave the E.M.F. of a cadmium cell at  $20^\circ$  as 1.0184 volts, and the ratio *Clark*  $15^\circ$ /*cadmium*  $20^\circ$  = 1.4066, whence the E.M.F. of the Clark cell at  $15^\circ$  = 1.4326. The mean E.M.F. is 1.4328 volts at  $15^\circ$  and 1.4492 volts at  $0^\circ$ .

The author has previously determined the absolute value of the E.M.F. of a Clark cell at  $0^\circ$  by means of Helmholtz's electrodynamicometer, and obtained the value  $E = 1.4488$  volts (*Ann. Phys. Chem.*, 1896, [ii], 59, 532); if this be taken as a standard, the electrochemical equivalent of silver is found to be 1.1183 mg. per coulomb.

T. M. L.

**Electromotive Force required to Decompose Electrolytes**  
By EMIL BOSE (*Zeit. Elektrochem.*, 1898, 5, 153—177).—Further experiments on the lines of those of Glaser (this vol., ii, 78) are described; improvements in the experimental technique give the determinations greater accuracy than before. In a typical case, the curve connecting current and applied E.M.F. would consist of an almost horizontal line below the decomposition point, and of a more or less rapidly rising one above it. In reality, the two lines are joined by a curved portion instead of meeting at a sharp angle, and when the concentration of the ion which is being eliminated is small, the curve rises at first after the decomposition point is passed and then falls again. These peculiarities are shown to be due to changes of concentration near the small electrode. In solutions containing bromine and chlorine ions, the current increases so rapidly after the E.M.F. necessary for the separation of bromine is exceeded, that the further rise due to the separation of chlorine is not observed unless the concentration of the bromine ions is so small that the above mentioned

fall occurs above the decomposition point for bromine. In all cases, a smaller E.M.F. is required to separate an ion from a concentrated solution than from a dilute one. The phenomena observed in separating silver and hydrogen ions from a solution of silver sulphate in dilute sulphuric acid, and silver and copper ions from an acid solution, were quite analogous to the foregoing. Copper ions require the same E.M.F. for their separation from solutions in sulphuric or in nitric acid. In this case, there are two decomposition points, due doubtless, to cuprous and cupric ions respectively, one of which lies about 0.1 volt above the other. Both points are displaced to the same extent by a change of concentration. This latter circumstance indicates that the equilibrium between them is represented by the equation  $\text{Cu} + \overset{++}{\text{Cu}} \rightleftharpoons \overset{+}{\text{Cu}} - \overset{+}{\text{Cu}}$ .

Attempts to measure the E.M.F. required to separate mercurous ions from mercurous nitrate, using an oxygen saturated anode, gave values much lower than those calculated from the E.M.F. of galvanic cells. The discrepancy was traced to the rapid depolarisation of the oxygen anode by the mercurous nitrate solution.

Glaser's observation that, using a hydrogen cathode, 1.08 volts are required to separate  $\text{O}^-$  ions from normal solutions of caustic soda or of sulphuric acid is confirmed. This point is not well marked, as is always the case where gaseous products are formed.

A very careful series of determinations of the E.M.F. required to separate silver ions from their charges, using a large platinised platinum anode saturated with oxygen at atmospheric pressure, gave the following results:—The concentrations of the solutions in grammols. per litre were: I,  $1.75\text{AgNO}_3 + \text{HNO}_3$ . II,  $0.175\text{AgNO}_3 + \text{HNO}_3$ . III,  $0.0175\text{AgNO}_3 + \text{HNO}_3$ . IV,  $0.00175\text{AgNO}_3 + \text{HNO}_3$ . V,  $0.000175\text{AgNO}_3 + \text{HNO}_3$ .

Temp.	I.	II.	III.	IV.	V.
0°			0.3452	0.3875	0.4528
20	0.2982	0.3205	0.3682	0.4255	0.4845
35	0.3041	0.3371	0.3916	0.4503	
50	0.313				

The increase of E.M.F. accompanying the dilution is in satisfactory agreement with that deduced from Nernst's theory.

The anodic decomposition points of a number of acids are also determined with reference to a hydrogen cathode. They all exhibit a first decomposition point at 1.67 volts, corresponding with the separation

of  $\text{OH}^-$  ions. The monobasic acids have one, and the dibasic acids two, other decomposition points at higher E.M.F.'s. In a few cases, the first decomposition is found much below 1.67 volts, owing to cathodic depolarisation; with chromic acid, this is especially well marked. Oxalic acid is exceptional; it gives a first decomposition point at

1 volt (due possibly to  $\bar{\text{C}}_2\bar{\text{O}}_4$  ions), a second at 1.67 volts, due to OH ions, and a third at 2.15 volts, due possibly to  $\text{COOH}\cdot\text{COO}$  ions. The paper concludes with a theoretical discussion of the changes of concentration, produced by the current in the neighbourhood of the electrodes and of their effect on the forces opposing the separation of the ions in the neutral state. T. E.

**Electrolytic Behaviour of some Complex Fluorides and Oxyfluorides.** By ARTURO MIOLATI and UGO ALVISI (*Real. Accad. Linc.*, 1897, ii, 376—381).—According to Werner, whose views on the constitution of inorganic compounds are briefly discussed, the number of groups or atoms with which an element is capable of uniting to form a complex ion never exceeds six. The formulæ of not a few compounds appear to contradict this theory, and the electric conductivity of some of these have been determined, in order to ascertain whether they really form exceptions to the rule. By the large increase of the conductivity with increasing dilution, the salts  $(\text{MoO}_2\text{F}_5)(\text{NH}_4)_3$  and  $(\text{SiF}_7)(\text{NH}_4)_3$  are shown to undergo hydrolytic dissociation, whereas the results obtained in the case of the compounds  $(\text{UO}_2\text{F}_5)\text{K}_3$  ( $\mu_{1024-32} = 29.6$ ,  $\mu_\infty = 133.5$ ) and  $(\text{UO}_2\text{F}_5)(\text{NH}_4)_3$  ( $\mu_{1024-32} = 29.1$ ,  $\mu_\infty = 133.1$ ) indicate the existence of stable complex ions, the composition of which is not readily reconcilable with Werner's views. The behaviour of the salts  $\text{TiF}_6(\text{NH}_4)_2$ ,  $\text{MoO}_2\text{F}_3(\text{NH}_4)$ ,  $\text{MoO}_2\text{F}_4(\text{NH}_4)_2$ ,  $\text{MoO}_2\text{F}_4\text{K}_2$ , and  $\text{WO}_2\text{F}_4\text{K}_2$  has also been studied, but as they are all decomposed by water to a greater or less extent, the results are considered to be of little value. N. L.

**Conductivity of Electrolytes in Organic Solvents.** By PAUL DUTOIT and L. FRIDERICH (*Bull. Soc. Chim.*, 1898, [iii], 19, 321—337).—In order to obtain further knowledge of the relations which previous work (Abstr., 1897, ii, 546) has shown to exist between the conductivity of solutions and the properties of the solvent, the authors have investigated solutions of various electrolytes in acetone, acetophenone, acetonitrile, propionitrile, and butyronitrile. The conductivities were determined by Kohlrausch's method, the coefficients of viscosity by Ostwald's method, and the degree of association of the solvents by the method devised by Ramsay and Shields, which is based on a determination of the molecular surface energy. Full experimental details are given in the paper. For several electrolytes in acetonitrile and acetone solution, higher values are found for the molecular conductivity at infinite dilution than are observed in the case of aqueous solutions. This is especially the case with acetonitrile, a fact which is in perfect accordance with the high degree of polymerisation and the low coefficient of viscosity of this liquid. The behaviour of the binary electrolytes examined is quite analogous to that observed with aqueous solutions, the conductivity increasing with the dilution in accordance with Ostwald's law of dilution; the values obtained for  $\mu_\infty$  are of the same order of magnitude, and the temperature coefficients are normal. In the case of the ternary electrolytes, however, the conductivity is low, not exceeding a fourth

of the values found for binary electrolytes, and the behaviour of cadmium iodide is particularly abnormal. The molecular conductivity of the latter varies neither with the dilution nor with the temperature, and it is suggested that combination of the salt with the solvent may possibly occur. From a consideration of the results obtained by the authors and by other experimenters, the general conclusion is reached that when the same electrolyte is dissolved in different solvents, the values obtained for  $\mu_{\infty}$  are direct functions of the degree of polymerisation, and inverse functions of the coefficient of viscosity of the solvent.

N. L.

**Fluidity and Electrolytic Conductivity of Salt Solutions, and the Conductivity of Oleic Acid and the Oleates.** By RUDOLF DENNHARDT (*Ann. Phys. Chem.*, 1899, [ii], 67, 325—344).—Ammonium nitrate, chloride, and bromide, and potassium bromide, iodide, chloride, and nitrate, show maxima of fluidity in aqueous solution (Sprung, *Ann. Phys. Chem.*, 1876, 159, 399), but no such maxima are found in the conductivity; all these salts behave according to the ordinary law of dilution, except potassium bromide and iodide, the conductivity curves of which show a reversal of curvature.

Solutions of oleic acid in methylic alcohol show maxima of contraction at about 15 and 50 per cent., in ethylic alcohol at about 5 and 50 per cent., and in amylic alcohol at about 14 per cent. The specific conductivity exhibits a maximum at about 20 per cent. in methylic alcohol, and at 35 per cent. in ethylic alcohol, but a minimum in amylic alcohol at about 14 per cent. The molecular conductivity also exhibits maxima at 18 and 36 per cent. respectively in methylic and ethylic alcohols, and the temperature coefficients show minima at the same concentrations. The conductivity of alcoholic solutions of oleic acid increases slightly on keeping.

Aqueous solutions of sodium and potassium oleates differ from all other electrolytes in that the molecular conductivity exhibits a minimum value; for the potassium salt, this occurs at  $c=0.03$  at  $0^{\circ}$ , and  $c=0.01$  at  $60^{\circ}$ , and for the sodium salt at  $c=0.01$  at  $18^{\circ}$  and  $44^{\circ}$ . The specific conductivity increases with the concentration, but more rapidly in concentrated than in dilute solutions, so that the conductivity-concentration curve is convex towards the axis of concentration; the abnormal increase which occurs is shown by comparison with potassium chloride, since at  $c=0.01$  the oleate has only one-third the conductivity of the chloride, whilst at  $c=0.1$  it is greater by one-half. No such minimum is found in alcoholic solutions, although an alteration in the curvature of the conductivity curve occurs at  $c=0.01$ ; the conductivity is greater in a solution in methylic than in ethylic alcohol, but is less in an amylic alcohol solution.

The author explains the abnormal behaviour of aqueous solutions of the oleates as due to hydrolytic dissociation into an acid oleate and caustic soda, and at greater dilution into oleic acid and caustic soda.

T. M. L.

**Alloys of Iron and Nickel.** By FLORIS OSMOND (*Compt. rend.*, 1899, 128, 304—307).—The following table (compare Abstr., 1894,

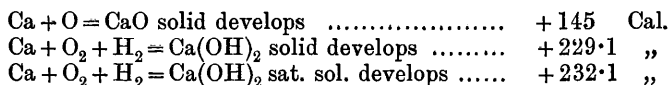
ii, 283) gives the points of transformation of alloys of nickel and iron of varying composition.

Composition.			Disappearance of magnetism during heating.	Appearance of magnetism during cooling.
C.	Mn.	Ni.		
0·19	0·79	0·27	735°	715°
0·19	0·65	3·82	710	628
0·17	0·68	7·65	710	530
0·23	0·93	15·48	623	145
0·16	0·32	24·75	540	27
0·61	0·46	26·20	0	below 0
0·23	0·49	31·44	138	124
0·46	0·28	35·70	276	232
0·30	0·68	43·04	401	357
0·11	0·38	58·30	557	523
0·08	0·41	69·20	590	557
0·07	0·68	76·75	582	545
0·12	0·38	88·95	488	457
0·09	0·74	92·20	450	415
0·10	0·86	94·70	425	388
0·12	0·55	98·50	384	345

When the transformation temperatures for both cooling and heating are plotted against percentages of nickel, curves are obtained which in each case consist of three branches; these are widely separated for proportions of nickel between 0 and 25 per cent., but for greater percentages they lie closely together. In the heating curve, a wide break exists between the points corresponding with 24·75 and 26·20 per cent. of nickel. The minimum transformation temperature probably corresponds with the existence of an eutectic alloy, and the maximum with that of a partially dissociated compound,  $\text{Ni}_2\text{Fe}$ .

W. A. D.

**Heat of Formation of Calcium Oxide.** By HENRI MOISSAN (*Compt. rend.*, 1899, 128, 384—387).—Crystallised calcium was enclosed in a small perforated platinum cylinder and immersed in water, which, under these conditions, attacks it regularly but completely,  $\text{Ca} + 2\text{H}_2\text{O} = \text{H}_2 + \text{Ca}(\text{OH})_2$  sat. sol., develops + 94·10 Cal. and hence,



The heat of formation of calcium oxide is higher than that of potassium or sodium oxides, and therefore, as the author has already shown, the former metal should displace either of the two latter; it is also somewhat higher than that of lithium oxide (+ 141·2 Cal.) and the author finds that calcium will displace lithium at a dull red heat. The fact that calcium will not displace magnesium from its oxide indicates that Thomsen's value (+ 143·4 Cal.) for the heat of formation of magnesium

oxide is too low ; his value for the heat of formation of calcium oxide is lower than that found by the author. C. H. B.

**Thermochemistry of Azelaic Acid.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1898, [iii], 19, 301—302).—The azelaic acid examined was obtained by the oxidation of castor oil, and after careful purification melted at  $106.2^{\circ}$ . The solubility in water of potassium hydrogen azelate is so small that its heat of dissolution could not be determined. The heat of dissolution of the normal salt, which crystallises with  $1\text{H}_2\text{O}$ , is  $+1.87$  Cal. ; when heated at  $115^{\circ}$ , it becomes anhydrous, and then dissolves in water with the development of  $+4.91$  Cal. From the heat of neutralisation,  $\text{C}_9\text{H}_{16}\text{O}_4(\text{solid}) + 2\text{KOH}(\text{diss.}) = \text{C}_9\text{H}_{14}\text{K}_2\text{O}_4(\text{diss.}) + 18.66$  Cal., it is calculated that the heat of formation of normal potassium azelate is  $41.53$  Cal., all the substances concerned being in the solid state. This result is lower than that obtained in the case of suberic acid ( $44.76$  Cal.) and sebacic acid ( $43.99$  Cal.), but since the azelaic acid examined is not the normal acid, which has been variously stated to melt at temperatures ranging between  $114^{\circ}$  and  $118^{\circ}$ , it cannot properly be compared with the normal acids of the oxalic series which the author has previously studied (this vol., ii, 80). N. L.

**Cryoscopic Behaviour of Orthonitrophenol.** By G. AMPOLA and C. RIMATORI (*Real. Accad. Linc.*, 1897, ii, 31—33).—Determinations of the depression of the freezing point of solutions of bromoform, veratrole, paraxylene, toluene, pyridine, aniline, phenol, thymol, isobutylic alcohol, tertiary butylic alcohol, benzylic alcohol, isobutyric acid, and acetic acid in orthonitrophenol show that the behaviour of the latter is analogous to that of phenol, normal depressions being obtained with neutral and basic substances, alcohols, and phenols, whilst acids behave abnormally. The mean molecular depression was found to be  $74.37$ . In no case does the molecular depression increase with the concentration, as happens with ethylic veratrole oxalate in phenol, but always decreases with a rapidity greater than that found by Paternò with phenol solutions. N. L.

**Heat of Formation of Sodium Meta- and Para-hydroxybenzoates.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1898, [iii], 19, 250—251).—The author finds that the heat of dissolution of sodium metahydroxybenzoate is  $+0.26$  Cal., and of the corresponding para-salt  $+0.32$  Cal. ; from these values and those given by Berthelot and Werner (*Abstr.*, 1885, 1032) for the heats of neutralisation of the hydroxybenzoic acids, it follows that the action  $\text{C}_7\text{H}_6\text{O}_3 \text{ sol.} + \text{NaOH sol.} = \text{C}_7\text{H}_5\text{O}_3\text{Na sol.} + \text{H}_2\text{O sol.}$  develops  $+17.77$  Cal. in the case of the meta-acid and  $+17.79$  Cal. in the case of the para-acid. W. A. D.

**Thermal Study of the Hydroxybenzoic Acids: Influence of the Phenolic Hydroxyl.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1898, [iii], 19, 249—250).—The heats of formation of the solid sodium hydroxybenzoates produced according to the reaction  $\text{acid sol.} + \text{NaOH sol.} = \text{salt sol.} + \text{H}_2\text{O sol.} + Q.$ , are as follows: sodium salicylate  $+19.15$  Cal., sodium metahydroxybenzoate  $+17.77$  Cal., and the parahydroxybenzoate  $+17.79$  Cal. Since the

heat of formation of solid sodium benzoate is +17.40 Cal., it follows that, although the phenolic hydroxyl enhances the acidimetric value of the carboxyl group in the case of the ortho-acid, it is almost without influence in those of the meta- and para-acids. These results are thus analogous to those already obtained by introducing a nitro- or a carboxyl group in different positions relatively to the carboxyl group of benzoic acid (*Ann. Chim. Phys.*, 1894, [vii], 1, 145, and Abstr., 1895, ii, 202).

W. A. D.

**Heat of Vaporisation of Piperidine, Pyridine, Acetonitrile, and Capronitrile.** By WLADIMIR F. LUGININ (*Compt. rend.*, 1899, 128, 366—369).—The determinations were made by the author's method at an altitude of 600 m. and under the atmospheric pressure of 715 to 725 mm.

*Piperidine*: specific heat between 19.5° and 97.5° = 0.5233; heat of vaporisation, -88.92 Cals.

*Pyridine*: specific heat between 21.5° and 107.6° = 0.4315; heat of vaporisation, -101.39 Cals.

*Acetonitrile*: specific heat between 20.7° and 76.4° = 0.5408; heat of vaporisation, -170.68 Cals.

*Capronitrile*: specific heat between 18° and 155.5° = 0.5417; heat of vaporisation, -88.09 Cals.

In all cases, the quotient, molecular weight  $\times$  latent heat of vaporisation/absolute boiling point is about 20.0, and this indicates that the liquids consist of non-polymerised molecules—a conclusion previously arrived at by Ramsay and Shields in the case of piperidine and pyridine, as a result of their measurements of the surface tensions of these liquids.

C. H. B.

**Thermal Conductivity of Liquids.** By EDMOND VAN AUBEL (*Zeit. physikal. Chem.*, 1899, 28, 336—341).—According to Weber, the thermal conductivity of a liquid is given by the expression  $k/c \cdot \sqrt[3]{V} = \text{const.}$  where  $k$  is the conductivity,  $c$  the thermal capacity of unit volume, and  $V$  the molecular volume. Lees' results (*Phil. Trans.*, 1898, 191, 399) afford data for testing this relationship, and the values of the above constants thus obtained are (1) at 11°: water, 0.00390; acetic acid, 0.00339; (2) at 32°: water, 0.00343; glycerol, 0.00381; water-glycerol, 0.00320, so that the law is at best only an approximation.

L. M. J.

**Researches on Gases.** By ANATOLE LEDUC (*Ann. Chim. Phys.*, 1898, [vii], 15, 5—114).—A detailed account of work already published (compare Abstr., 1897, ii, 133, 140, 549; 1898, ii, 20, 108, 215, 326, 331, 471).

G. T. M.

**Transition Points of Complex Systems as Fixed Points in Thermometry.** By THEODORE W. RICHARDS and JESSE BRIGGS CHURCHILL (*Zeit. physikal. Chem.*, 1898, 28, 313—316).—The authors have shown that the transition temperature of hydrated sodium sulphate is a convenient fixed point (Abstr., 1898, ii, 555); and Meyerhoffer and Saunders have also suggested the use of a mixture of sodium chloride and sodium sulphate for a normal room tempera-



ture (17.9°). The author considers it too low for this purpose (at least in America) and also that the use of a complex system is open to objection. The following transition temperatures may also be employed (temperatures given on hydrogen scale).

Sodium chromate .....	19.63°	Sodium bromide .....	50.7°
Sodium sulphate .....	32.38	Manganese chloride ...	57.7
Sodium carbonate .....	35.2	Trisodium phosphate	73.3
Sodium thiosulphate ...	47.9	Barium hydroxide ...	77.9

L. M. J.

### Solidification of Liquid Mixtures of Tautomeric Compounds.

By HENDRIK W. BAKHUIS ROOZEBOOM (*Zeit. physikal. Chem.*, 1899, 28, 289—301).—Curves of composition plotted against temperature are given to illustrate the possible phenomena of solidification in the case of tautomeric liquids. The melting point curve consists of two lines, *AC*, *BC*, meeting in the eutectic point *C*. At higher temperatures are transition curves giving the final equilibrium composition when either of the compounds  $\alpha$  and  $\beta$  is heated; these curves meet at a point *F*, above which only one liquid mixture is possible at any particular temperature. If a mixture is heated to a temperature  $x$  above *F* and rapidly cooled, the product first separating corresponds with that for the concentration at the point  $x$ , and finally the eutectic mixture results; if slowly cooled, however, the composition changes until the point *F* is reached and the product which separates first depends only on the composition at the point *F*. Similar cases, in which the temperature is not raised to the true equilibrium temperature of *F*, are considered, and are easily derived from the diagram. If the two liquids are further capable of forming a solid compound, the only differences are those due to the different form of the melting point curve, which consists of three curves with two minima in place of two curves with but one minimum.

L. M. J.

Temperature Coefficients of Solutions of Salts in Mixtures of Alcohol and Ether. By CARLO CATTANEO (*Real. Accad. Linc.*, 1897, ii, 89—94).—In view of the fact, previously noticed by the author and since confirmed by other observers, that ethereal saline solutions are peculiar inasmuch as the electric conductivity decreases with rise of temperature, it seemed of interest to ascertain whether, by using a mixture of alcohol and ether as the solvent, solutions could be obtained having a conductivity independent of the temperature. A series of determinations made with ferric chloride shows that the point at which the temperature coefficient becomes zero depends, not only on the relative proportions of alcohol and ether, but also on the concentration. Thus, with solutions containing about 0.1 per cent. of ferric chloride, the neutral point is reached when the weights of ether and alcohol are in the proportion of 100 to 71—72, whilst with stronger solutions (about 1 per cent.) the ratio is 100 to 59—63. It is also shown that, in a long series of determinations, considerable errors may be introduced owing to evaporation of the solution and absorption of water from the air. Some experiments with auric chloride indicate that the neutral point is reached with a relatively smaller proportion of alcohol than is required in the case of ferric chloride.

N. L.

**Reciprocal Solubilities of Liquids; Vapour Pressure and Critical Points of Mixtures.** By J. P. KUENEN and W. G. ROBSON (*Zeit. physikal. Chem.*, 1899, 28, 342—365).—Rothmund has shown that in some cases of mutually soluble mixed liquids an upper, and in others a lower, critical temperature occurs at which the liquids are miscible, whilst in a few cases evidence was obtained of the probable existence of both points in a mixture (Abstr., 1898, ii, 503), and has led to the suggestion that the general form of the solubility curve is a closed curve. The system, however, is a three-phase system, and the critical point of the vapour phase and upper liquid may be reached before that of the two liquids, a case not considered by Rothmund. The forms of curves so obtainable are given, and in order to investigate such cases, the author determined the vapour pressure at temperatures reaching to the critical point in the case of various mixtures. With ether and water, an upper critical point for vapour and liquid was reached at  $201^{\circ}$ ; the vapour pressure of the system was at all temperatures higher than that of the ether but less than the sum of the ether and water pressures. Mixtures of ethane and various alcohols were next examined. With methylic alcohol, the pressure of the system was at all temperatures intermediate between those of the two constituents, and hence the composition of the vapour does not lie between those of the two liquid phases; the critical point was reached at  $35\cdot37^{\circ}$ . With ethylic alcohol, a lower critical point was found at  $31\cdot9^{\circ}$  and a vapour | liquid critical point at  $40\cdot67^{\circ}$ ; with propylic alcohol, these temperatures become  $38\cdot67^{\circ}$  and  $41\cdot7^{\circ}$ , whilst with butylic alcohol they are  $38\cdot1^{\circ}$  and  $39\cdot8^{\circ}$ . In the case of the mixture with propylic alcohol, it was observed that increase of pressure could cause miscibility of the two liquid phases after condensation of the vapour phase. Mixtures with isopropylic alcohol behave similarly, but the lower critical temperature could not be accurately determined, whilst for isoamylic alcohol a three-phase temperature interval could not be found. A miscible mixture of ethane and water could not be obtained and the vapour | liquid critical point is almost identical with that of pure ethane. For carbonic anhydride and water, the critical temperature is somewhat lower than that of the pure anhydride, as would be expected from the fact that the three-phase pressure is less than that of the anhydride. L. M. J.

**Phenomena of Physical Equilibrium in Mixtures of Isomorphous Substances.** By GIUSEPPE BRUNI (*Gazzetta*, 1898, 28, ii, 322—333).—The depressions of the freezing point of a series of solutions of different concentrations of naphthalene in the isomorphous  $\beta$ -naphthol were determined. From the results, it is concluded that Küster's law—which states that for mixtures of two perfectly isomorphous substances the freezing point curve coincides with the straight line joining the freezing points of the two components—does not hold, but that the freezing point of the mixture varies between those of the two components continuously, but not proportionately to the concentration.

Using mixtures of the same two compounds, the distribution of the two components between the liquid and solid phases has also been

determined, with results showing that the solid separating from the liquid mixture is richer in the component of higher melting point than the liquid. This is in direct opposition to the views of Küster, but is in complete accord with van't Hoff's general theory of solid solutions.

T. H. P.

**Significance of Osmotic Pressure in the Thermodynamics of Solutions.** By NICOLAI N. SCHILLER (*Ann. Phys. Chem.*, 1899, [ii], 67, 291—306).—A mathematical paper in which the author deduces expressions for the vapour pressure and heat of dilution of solutions, and for the heat of solution of gases.

T. M. L.

**Osmotic Pressure and Cryoscopy.** By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1898, [iii], 19, 102—106).—According to Crompton (*Trans.*, 1897, 925), van't Hoff's law requires modification in the case of associated solvents, and the osmotic pressure follows the equation  $PV = xRT$ , where  $x$  is the factor of association of the solvent. The author endeavours to show, by reasoning from fundamental principles, that the osmotic pressure is quite independent of the degree of association of the solvent, and contends that the facts adduced by Crompton in support of his theory are in full accordance with van't Hoff's law in its original form.

N. L.

**Osmotic Measurements.** By A. PONSOT (*Bull. Soc. Chim.*, 1898, [iii], 19, 9—10).—The mean of ten measurements of the osmotic pressure at 11.8° of a solution containing 1.235 grams of cane sugar per litre gave a value approximately equal to that calculated (870 mm.) on the assumption that the sugar is in the state of a perfect gas. It thus appears that, in very dilute, as well as in more concentrated, solutions (Pfeffer and Naccari), the coefficient  $i$  of van't Hoff's relation is equal to unity; and that Raoult's hypothesis of the dissociation of cane sugar in very dilute aqueous solution is not justified. This conclusion is supported by the cryoscopic values formerly obtained by the author (*Abstr.*, 1898, ii, 55), which give the value  $i = 1.004$ .

W. A. D.

**Relation between Osmotic Work and Osmotic Pressure.** By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1899, 28, 220—224).—The author has previously deduced an expression for the osmotic work, which may be stated as  $\pi = Pv_0/(1 + P/2k)$  (*Abstr.*, 1897, ii, 395). This leads to the equation  $dv = v_0(1 + P/2k)$ , but the volume alteration is not capable of direct measurement from the volume change on dilution. The usually accepted thermodynamical relation between vapour pressure and osmotic pressure is not strictly accurate, inasmuch as it is assumed that when water is added to an infinite bulk of solution the volume change is infinitely small, an erroneous assumption, for although the pressure change become zero, yet the volume change for infinite volume may still be finite. Dieterici's calculation of the osmotic pressure from the density changes during dilution are not free from a similar error, and it is shown that the volume changes due to the removal of solvent at constant concentration, as deduced by Dieterici (*Ann. Phys. Chem.*,

1893, [ii], 50, 67), do not agree with those calculated by the author's formula.  
L. M. J.

**Measurement of Viscosity Coefficients.** By PHILIPPE A. GUYE and L. FRIDERICH (*Bull. Soc. Chim.*, 1898, [iii], 19, 164—168).—Ostwald's apparatus is employed, and is calibrated by means of benzene, employing the viscosity constants obtained for this substance by Thorpe and Rodger (*Phil. Trans.*, 1894, 185, 397). The coefficients of viscosity determined for the following liquids, pentane, hexane, carbon bisulphide, chloroform, and ethylic bromide, agree closely with those obtained by these observers, that for ethylic iodide differs somewhat, but the discrepancy is probably due to impurity and to the unstable nature of the substance.

Liquids closely related to one another in chemical constitution differ only slightly in density, whereas the coefficient of viscosity varies considerably.  
G. T. M.

**Molecular Interchanges between Soluble Salts.** By E. ROCA (*Bull. Soc. Chim.*, 1898, [iii], 19, 132—134).—When solutions of two salts, MA and  $M_1A_1$ , are mixed in molecular proportions, partial double decomposition occurs, in general, with production of four salts, according to the equation,  $MA + M_1A_1 + Aq = (1 - m)MA + (1 - m)M_1A_1 + mM_1A + mMA_1 + Aq$ . The fraction  $m$  depends on the dilution and on the temperature, and if these are such that  $m$  tends towards, and ultimately becomes equal to, unity, complete decomposition occurs according to the equation  $MA + M_1A_1 = M_1A + MA_1$ . In certain cases, of which the preparation of potassium nitrate and potassium chlorate are examples, the salts finally produced admit of separation by crystallisation; very often, however, the separation is, for various reasons, incomplete. Thus, if a solution containing ammonium sulphate and sodium nitrate is concentrated by evaporation, about three-fourths of the theoretical amount of sodium sulphate is first deposited, and then all the salts present crystallise out together; it is, therefore, impossible to prepare ammonium nitrate in this way. The author finds, however, that if the solution is evaporated to dryness and the residue exhausted with alcohol of 95—96 per cent., the sodium sulphate remains practically undissolved, and pure ammonium nitrate is obtained by concentrating the solution. It is suggested that, by operating in this manner with suitable solvents, a number of separations might be effected.  
N. L.

**Energy of some Bases of Mixed Function.** By GIACOMO CARRARA and U. ROSSI (*Real. Accad. Linc.*, 1897, ii, 208—216).—The substance of this paper has appeared elsewhere (*Abstr.*, 1898, ii, 278).  
N. L.

**Velocity of Limited Reactions.** By PAUL TH. MULLER (*Bull. Soc. Chim.*, 1898, [iii], 19, 337—343).—The equation,  $dx/dt = k_1(A - x) - k_2x$ , representing a limited reaction of the first order, may be written  $dx/dt = (k_1 + k_2)(a - x)$ ; that is, the velocity of the reaction is equal to that of an unlimited reaction of the first order if the limit,  $a$ , of the substance is taken for the initial active mass. Similarly, for limited reactions of the second order, the usual equation may be written,

$dx/dt = (k_1 - k_2)(a - x)(b - x)$ , where  $a$  is the *chemical limit* of the reaction, and  $b$ , if positive, is numerically greater than  $a$ . The author has examined the results obtained by Berthelot and Péan de Saint-Gilles (*Ann. Chim. Phys.*, 1862, [iii], 19, 83), and, more recently, by Knoblauch (Abstr., 1897, ii, 311), in studying the etherification of acetic acid and the hydrolysis of ethylic acetate, and finds that the course of the reactions is quite as well represented by the simple equation,  $dx/dt = \lambda(a - x)$ , where  $\lambda$  is constant, as by the more complex equation,  $dx/dt = (k_1 - k_2)(a - x)(b - x)$ . Since, however, in the reactions referred to,  $b$  is numerically much greater than  $a$ , the variations in the factor  $(b - a)$  are very small, and in order to decide definitely between the two equations, it will be necessary to study reactions in which  $b$  exceeds  $a$  to as small an extent as possible. N. L.

**Velocity of Reaction.** By ALEXANDER VON HEMPTINNE and A. BEKAERT (*Zeit. physikal. Chem.*, 1899, 28, 225—240).—The influence of various media on the velocity of reaction of ethylic bromide with triethylamine was determined, the solvents employed being benzene, xylene, chlorobenzene, acetone, and methylic, ethylic, propylic, and benzylic alcohols with various mixtures of these liquids. It was found that, in mixtures of compounds of a similar nature, such as two alcohols, the velocity of reaction could be approximately calculated from that in each constituent, but in mixtures containing an alcohol with some other liquid, the velocity far exceeded that calculated from a mixture rule. The temperature coefficients, as deduced from the results obtained by the author and by Menshutkin, are approximately equal for benzene, acetone, chlorobenzene, and xylene, but are markedly less for the alcohols. A few ternary mixtures were also examined, and although the velocity was not calculable from those in the three constituents, fair agreement was obtained when calculated as a binary system,  $A + (B + C)$ . L. M. J.

**Chemical Reaction Velocities.** By SVANTE ARRHENIUS (*Zeit. physikal. Chem.*, 1899, 28, 317—335).—The author has previously suggested that many reactions such, for example, as the inversion of cane sugar, are brought about only with certain 'active' molecules, and that equilibrium exists between these active and the inactive molecules (Abstr., 1889, 1003). The enormous influence of the temperature on the velocity of inversion is most probably due to change in the number of active molecules. The velocity of inversion increases with the concentration of the sugar, and the author points out that this increase is approximately proportional to the increase of osmotic pressure per gram-molecule, and hence it is this osmotic pressure, and not the actual concentration, which should be considered in deducing reaction velocities. As foreign substances in general increase the osmotic pressure of a compound, they should also in general accelerate the velocities of reaction, which is actually the case. The velocity of inversion of sugar by acids is diminished by the addition of alcohol, but this does not necessitate a decrease of dissociation, as it could be also brought about by a change in the number of active molecules which is probably decreased by the alcohol just as the dissociation of weak electrolytes is diminished. There

is no reason, therefore, to assume that conductivity experiments yield wrong values for the dissociation (Abstr., 1898, ii, 158), whilst Goldschmidt's values for the solubilities of silver acetate, propionate, and isobutyrate are in good accord with those calculated, if a correction which he overlooked (Abstr., 1898, ii, 152) is made for the change of dissociation with concentration. L. M. J.

**Gases of the Argon-Helium Type, and the Periodic System.** By BOHUSLAV BRAUNER (*Ber.*, 1899, 32, 708—712).—The author discusses reasons for regarding the newly-discovered gases of the argon-helium type as inactive compounds or allotropic modifications rather than new elements. M. O. F.

**Crystalline-Liquids.** By RUDOLF SCHENCK (*Zeit. physikal. Chem.*, 1899, 28, 280—288).—Crystalline-liquids are regarded by Lehmann as crystals of extraordinarily small viscosity, whilst by Quincke (*Ann. Phys. Chem.*, [ii], 53, 613) they are considered to consist of a multitude of minute, solid crystallites, each enclosed in a thin liquid film. If this were the case, that is, if the liquid crystals were not homogeneous, different transition temperatures should be found for different preparations and for the products crystallised from different solvents. Parazoxyanisole was crystallised from (1) acetone, (2) alcohol, (3) chloroform, without any appreciable change of the transition point and the author hence considers Lehmann's view to be correct. Ostwald has suggested that the stability interval of crystalline-liquids must be near the critical point for solid and liquid, that is, the temperature at which the heat of fusion is zero. From the specific heats of the crystalline and isotropic liquids, the difference between the transition and critical temperatures is calculated as (1) 27.6° and (2) 18.4°; the difference in the values is perhaps due to dimorphism of the compound, and the author considers that similar determinations with other compounds are desirable (compare Abstr., 1898, ii, 286, 563). L. M. J.

**Molecular Weights of some Inorganic Salts.** By NICOLA CASTORO (*Gazzetta*, 1898, 28, ii, 317—322).—The author has determined the molecular weights of several inorganic salts by the freezing point method, using as the solvent urethane, for which the molecular depression of freezing point has been found by Eyckmann to be 49.6°. At the melting point of urethane (about 49°), the molecular weights of silver nitrate and of mercuric, cadmium, zinc and stannous chlorides are in accordance with the ordinary formulæ, but cobalt and cupric chlorides have double molecular weights, corresponding with the formulæ  $\text{Co}_2\text{Cl}_4$  and  $\text{Cu}_2\text{Cl}_4$ . Manganese chloride in dilute urethane solution shows a tendency to polymerise, the molecular weight being greater than the calculated value and increasing proportionally with the concentration. Acetamide was also tried as a solvent for inorganic salts, but the results were unsatisfactory. T. H. P.

**Absorption of Water Vapour by Compounds and its Partition between two Similar and two Dissimilar Substances.** By W. BUSNIKOFF (*Chem. Centr.*, 1898, i, 492—494, 649—651; from *J. russ. chem. Ges.*, 29, 482—524).—The rate of absorption of water

by sulphuric acid was determined by placing the acid in a Plattner's desiccator containing water and weighing from time to time. The variations of temperature (from 18—23°) during the experiment appeared to have no influence on the character of the results. In the first experiment, in which 2.0638 grams of sulphuric acid of a composition corresponding with  $\frac{1}{2}\text{H}_2\text{SO}_4 + 0.187\text{H}_2\text{O}$  were used, the acid acquired the composition of the hydrate,  $\text{H}_2\text{SO}_4 + 0.5\text{H}_2\text{O}$ , in 1.4 hours, of  $\text{H}_2\text{SO}_4 + 1\text{H}_2\text{O}$  in 3.9 hours, and of  $\text{H}_2\text{SO}_4 + 1.5\text{H}_2\text{O}$  in 6.7 hours. In the second experiment, in which 7.2814 grams of acid, corresponding with  $\text{H}_2\text{SO}_4 + 0.337\text{H}_2\text{O}$ , were used, the acid attained the composition  $\text{H}_2\text{SO}_4 + 0.516\text{H}_2\text{O}$  in 4 hours,  $\text{H}_2\text{SO}_4 + 1.140\text{H}_2\text{O}$  in 16 hours,  $\text{H}_2\text{SO}_4 + 1.242$  in 18 hours, and  $\text{H}_2\text{SO}_4 + 2.792\text{H}_2\text{O}$  in 76 hours. The results show that the rate of absorption of water up to the formation of the hydrate,  $\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$ , increases as the composition approaches that of a definite hydrate and then, after the formation of the hydrate, again decreases.

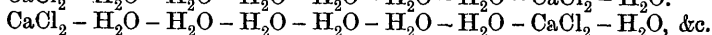
From experiments made by placing two portions of sulphuric acid of different concentrations in the same desiccator, it was found that the system did not attain a state of equilibrium until both liquids had acquired the same degree of hydration and then only if a definite hydrate could be formed. The amount, and perhaps also the rate, at which water is lost (or gained) is not dependent on the absolute quantity of the hydrate, but on its molecular weight.

The rate of absorption of water by calcium chloride was determined in the same way as in the case of sulphuric acid. The calcium chloride was melted in a stream of hydrogen chloride, and then brought into the desiccator; it forms an opalescent mass, in which crystals separate if moisture is excluded. If the limit of the formation of the hexahydrate is attained, no more crystals are formed. As in the case of sulphuric acid, the rate of absorption of water increases as the composition of a hydrate is approached, and then again decreases, and the break in the continuity of the curve lies between  $\text{CaCl}_2 + 10\text{H}_2\text{O}$  and  $\text{CaCl}_2 + 11\text{H}_2\text{O}$ . In an experiment in which 6.3376 grams of  $\text{CaCl}_2 + 0.820\text{H}_2\text{O}$  and 6.2872 grams of anhydrous calcium chloride were placed in the same desiccator, the composition of the former after 579 hours corresponded with  $\text{CaCl}_2 + 0.794\text{H}_2\text{O}$ , and that of the latter with  $\text{CaCl}_2 + 0.127\text{H}_2\text{O}$ . According to the author, there is a "critical hydrate," which is formed when the substance changes from the solid to the liquid state, and constitutes a point of demarcation between the absorption and the liberation of water.

In a system in which 10.3096 grams of  $\text{CaCl}_2 + 33.12\text{H}_2\text{O}$  and 21.7316 grams of 96.67 per cent. sulphuric acid were placed in the same vessel, equilibrium was attained after 623 hours, and the composition of the liquids corresponded with  $\text{CaCl}_2 + 2\text{H}_2\text{O}$  and  $2\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$  respectively. When 2.0638 grams of 96.67 per cent. sulphuric acid, which had been allowed to absorb 4.8274 grams of water and 6.8278 grams of anhydrous calcium chloride, were used, the system was in equilibrium after 2230 hours, and the liquids had the compositions  $\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$  and  $\text{CaCl}_2 + 3\text{H}_2\text{O}$  respectively.

Similar results were obtained with barium chloride and sulphuric acid, and with magnesium chloride and sulphuric acid.

According to the author, the molecules forming the hydrates are arranged symmetrically, so that a section of the mass of the hydrate  $\text{CaCl}_2 + 6\text{H}_2\text{O}$  would appear thus :



The crystalline form of the compound may depend on the angle between the corresponding molecules. The results show that the hydrates lose water when their molecular tension is greater than the tension of the surrounding water vapour, or *vice versa*. E. W. W.

**Oxygen Æolopile.** By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1899, 38, 102—103).—This apparatus is very similar to the Russian blast lamp. A spherical wrought iron vessel is furnished with a long tubular neck which is so bent that its open end is immediately below the bottom of the vessel, points horizontally, and is narrowed to a blow-pipe orifice. The vessel contains a mixture for generating oxygen, and is heated by a suitable lamp. The jet of oxygen deflects a portion of the lamp flame, and furnishes a powerful horizontal blow-pipe flame; should a vertical flame be desired, a fireclay cone bent at right angles is placed in front of the jet. M. J. S.

**Apparatus for Producing a Current of Warm Water of Constant Temperature.** By J. J. L. VAN RIJN (*Zeit. anal. Chem.*, 1899, 38, 96—99).—The principle made use of is identical with that of the ordinary hot water circulation apparatus employed in conservatories. A water reservoir, maintained at a constant temperature by a lamp controlled by a thermostat, is furnished with outflow and return pipes of caoutchouc, which are connected to the neighbouring instrument, the temperature of which is to be kept constant. M. J. S.

**Apparatus for the Separation of Organic Products.** By CAMILLE CHABRIÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 100—102).—This apparatus, of which a figure is given, is intended to facilitate the mechanical separation, by decantation, of liquids of different densities, or of liquids from solids. Provision is made for the exclusion of air, condensation of vapour, collection of evolved gases, agitation of the substances, and maintenance of a constant temperature. N. L.

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## Inorganic Chemistry.

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**Action of Acids on Iodic Acid and Iodates.** By PAUL CHRÉTIEN (*Ann. Chim. Phys.*, 1898, [vii], 15, 358—432).—The greater part of this work has already appeared (compare Abstr., 1896, ii, 651; 1897, ii, 138). Phosphoric acid partially dehydrates iodic acid without combining with it; but when iodic anhydride is added to hot phosphoric acid boiling at  $150^{\circ}$ , combination takes place, and on allowing the solution to cool, prismatic crystals of the complex acid,  $P_2O_5, 18I_2O_5, 4H_2O$ ,

separate. The salts of this acid are produced on adding iodic anhydride to a boiling solution of the corresponding phosphates in concentrated phosphoric acid; the following are obtained in this manner: *Potassium phosphiodate*,  $P_2O_5, 18I_2O_5, 4K_2O + 5H_2O$ , the *ammonium* salt of the same type crystallising with  $12H_2O$ , the *sodium* salt,  $P_2O_5, 18I_2O_5, 6Na_2O + 5H_2O$ , and the *lithium* salt,  $P_2O_5, 18I_2O_5, 3Li_2O + 11H_2O$ . Salts of this character could not be obtained with other metallic radicles.

Molybdiodic acid is obtained by dissolving molybdic dihydrate (2 mols.) in a dilute solution of iodic acid (1 mol.). Its salts are produced by the action of molybdic dihydrate on the corresponding iodates. The normal salts are of the type  $I_2O_5, 2MoO_3, RO$  (or  $R_2O$ ), and *potassium, ammonium, sodium, lithium, barium, strontium, calcium, magnesium, zinc, cobalt, nickel, copper, and silver* salts corresponding with this formula are described. The following *acid* salts have also been obtained  $(I_2O_5, 2MoO_3)_3, 4K_2O + 7H_2O$ ,  $(I_2O_5, 2MoO_3)_3, 2K_2O + 13H_2O$ ,  $(I_2O_5, 2MoO_3)_2, K_2O + 4H_2O$ ,  $(I_2O_5, 2MoO_3)_3, K_2O + 7H_2O$ ,  $(I_2O_5, 2MoO_3)_4, 3(NH_4)_2O + 6H_2O$ ,  $(I_2O_5, 2MoO_3)_4, 3SrO + 15H_2O$ ,  $(I_2O_5, 2MoO_3)_3, ZnO + 16H_2O$ ,  $(I_2O_5, 2MoO_3)_5, 2NiO + 15H_2O$ , and  $(I_2O_5, 2MoO_3)_5, CoO + 18H_2O$ . The *cadmium* and *manganese* salts correspond with the acid strontium salt, but crystallise with 15 and 9 of  $H_2O$  respectively. The *uranium* salt has the composition  $4I_2O_5, 3MoO_3, 2U_2O_3 + 3H_2O$ , and a complex *silver* salt,  $4I_2O_5, 3MoO_3, 4Ag_2O$ , is described.

The following derivatives of tungstiodic acid have been isolated: the *potassium* salt,  $2I_2O_5, 4WO_3, 2K_2O + 8H_2O$ , and the *ammonium* salt of like composition, but with  $12H_2O$ . G. T. M.

**Fluoriodates.** By RUDOLPH F. WEINLAND and O. LAUENSTEIN (*Zeit. anorg. Chem.*, 1899, 20, 30—39).—*Potassium difluoriodate*,  $KIO_2F_2$ , obtained by evaporating a solution of potassium iodate, or iodic acid and potassium fluoride, in 40 per cent. hydrofluoric acid, crystallises in colourless tablets belonging to the rhombic system,  $[a:b:c = 0.9925:1:1.4148]$ , and is isomorphous with ammonium iodate  $[a:b:c = 0.9948:1:1.4335]$ . It is stable in dry air and when kept under petroleum, but on exposure to the atmosphere decomposes into iodate and hydrogen fluoride; when heated in a tube, it melts to a colourless liquid, which quickly turns yellow and then decomposes into potassium fluoride with evolution of iodine, oxygen, and hydrogen fluoride. When treated with water, it dissolves, and is decomposed into potassium iodate and hydrofluoric acid; with warm sulphuric acid, it yields hydrofluoric acid, but concentrated sulphuric acid at  $10^\circ$  is without action on the salt. It is easily recrystallised from 40 per cent. hydrofluoric acid. Potassium di- and tri-iodates, when treated with hydrofluoric acid, are decomposed into iodic acid and the normal iodate, and the latter is then converted into the preceding salt. The author was unable to obtain double salts of potassium difluoriodate with alkali haloids.

*Ammonium difluoriodate* separates in rhombic crystals,  $[a:b:c = 0.9871:1:1.4107]$ , and is similar to the potassium salt. *Rubidium fluoriodate* is isomorphous with the preceding salts;  $[a:b:c =$

0.9855 : 1 : 1.4423]. *Cæsium difluoriodate*, obtained together with a salt containing more fluorine, which separates out first, crystallises in the rhombic system ;  $[a : b : c = 1.1765 : 1 : 0.5603]$ . The less soluble salt is apparently cæsium di-iodate, in which 2 oxygen atoms are replaced by 4 fluorine atoms ; it crystallises in hydrated forms, but has not yet been obtained in a pure state. *Sodium difluoriodate* crystallises in thin, six-sided tablets.

Fluoriodates of metals which form sparingly soluble fluorides cannot be prepared by the above method, and fluorides are formed with separation of iodic acid. Iodic acid dissolves easily in hydrofluoric acid without decomposition, and when the solution is evaporated to a syrup, the iodic acid crystallises out unaltered. Potassium bromate, when warmed with hydrofluoric acid, is partially decomposed, with formation of bromine and oxygen ; potassium chlorate crystallises without decomposition from hydrofluoric acid. E. C. R.

**Selenium and Tellurium Compounds.** By RENÉ METZNER (*Ann. Chim. Phys.*, 1898 [vii], 15, 203—288).—An account of work already published. (Compare Abstr., 1896, ii, 642 ; 1897, ii, 132, 169, 488, 489 ; 1898, ii, 572 ; and this vol., ii, 20). G. T. M.

**Synthesis of Hydroxylamine.** By AD. JOUVE (*Compt. rend.*, 1899, 128, 435—437).—When a mixture of 3 vols. of hydrogen with a little more than 2 vols. of nitric oxide is passed slowly over spongy platinum heated at 115—120°, a mixture of hydroxylamine and ammonia is formed. If the temperature is allowed to rise too high, or if the hydrogen is in excess, ammonia is the sole product, and in any case the yield of hydroxylamine is small. C. H. B.

**Inorganic Hydrazine Salts and the Preparation of Hydrogen Nitride.** By ALEXANDER SABANÉEFF (*Zeit. anorg. Chem.*, 1899, 20, 21—29).—*Hydrazine dithionate*,  $N_2H_4 \cdot H_2S_2O_6$ , prepared from hydrazine sulphate and barium dithionate, crystallises in long prisms, is easily soluble in water, and decomposes after a time. When the solution is allowed to evaporate over sulphuric acid, it decomposes with separation of sulphuric anhydride, and is converted into a mixture of hydrazine sulphate and the normal salt,  $2N_2H_4 \cdot H_2S_2O_6$  ; the latter is easily obtained by adding barium dithionate to a solution of hydrazine sulphate previously neutralised with hydrazine hydrate.

*Hydrazine amidosulphonate*,  $N_2H_4 \cdot HSO_3NH_2$ , is obtained by adding barium amidosulphonate to a neutral solution of hydrazine sulphate. The acid salt,  $N_2H_4(HSO_3NH_2)_2$ , could not be prepared, the products of the reaction being amidosulphonic acid and the normal salt.

The double salt,  $N_2H_4 \cdot NH_3 \cdot H_4P_2O_6$ , is obtained by neutralising a solution of hydrazine hypophosphate (Abstr., 1898, ii, 578) with ammonia, using methyl-orange as indicator. It separates in small crystals and is easily soluble in water.

[With A. SPERANSKY].—*Hydrazine pyrosulphite*,  $2N_2H_4 \cdot H_2S_2O_5$ , is obtained by passing sulphurous anhydride into an aqueous solution of hydrazine hydrate. When dissolved in water and neutralised with hydrazine hydrate, it is converted into the salt  $2N_2H_4 \cdot H_2SO_3$ . Both salts are easily oxidised and converted into the corresponding sulphates.

[With E. DENGIN.]—*Hydrazine nitrate*,  $\text{N}_2\text{H}_4\cdot\text{HNO}_3$ , obtained by neutralising hydrazine hydrate with nitric acid, using litmus as indicator, crystallises in long prisms when the syrupy solution is evaporated in a desiccator under diminished pressure, is somewhat soluble in absolute alcohol, crystallising from it in needles, has a faintly acid reaction, melts at  $69^\circ$ , begins to volatilise at  $140^\circ$ , is not decomposed at  $300^\circ$ , and explodes when heated over a free flame. When treated with concentrated sulphuric acid, a violent evolution of nitric oxide takes place; at  $-16^\circ$ , however, there is no reaction, and when warmed with dilute sulphuric acid, hydrogen nitride is formed. It reacts violently with phosphorus pentachloride, and is converted into hydrazine hydrochloride. The *acid nitrate*,  $\text{N}_2\text{H}_4\cdot 2\text{HNO}_3$ , obtained from barium nitrate and hydrazine sulphate, or by half neutralising hydrazine hydrate with nitric acid, crystallises in aggregates of needles or plates and is very unstable. When treated with absolute alcohol, it is converted into the normal salt. On heating rapidly, it melts at  $103\text{--}104^\circ$ , but begins to decompose at  $80^\circ$  when slowly heated, the products of the decomposition at  $80\text{--}85^\circ$  being hydrogen nitride, nitric acid, nitrogen, water, hydrazine nitrate, and ammonium nitrate. When heated on the water-bath, it yields hydrogen nitride (8 per cent.), nitric acid, nitrogen, and water, and a residue of ammonium nitrate, and when allowed to remain in a desiccator over sulphuric acid at the ordinary temperature, it decomposes into hydrogen nitride, hydrazine nitrate, and ammonium nitrate.

Hydrogen nitride is very easily prepared by cautiously warming a mixture of hydrazine sulphate (1.5 grams) and nitric acid of sp. gr. 1.3 (4 c.c.), and passing the gas into a solution of silver nitrate; the yield amounts to 10—12 per cent. of the weight of hydrazine sulphate employed.

E. C. R.

**Decomposition of Carbonic Oxide in Presence of Metallic Oxides.** By O. BOUDOUARD (*Compt. rend.*, 1899, 128, 307—309).—The author has studied the rate of oxidation of carbonic oxide when passed over heated nickel and cobalt oxides at  $445^\circ$ , and finds that, in both cases, it is much more rapid than when ferric oxide is employed (this vol., ii, 287); as in the latter case, the amount of decomposition increases with the quantity of oxide used and with the time. In all these cases, the amount of carbon deposited is of the same order of magnitude as that of the oxide employed; when a large excess of purified carbon is mixed with the oxide, the results obtained are, on the whole, the same as those already described, but the action appears to take place more slowly.

W. A. D.

**Chlorination of Carbon Bisulphide in Presence of Aluminium Chloride.** By A. MOUNEYRAT (*Bull. Soc. Chim.*, 1898, [iii], 19, 262—263).—When a current of dry chlorine is passed into a cold mixture of carbon bisulphide (300 grams) with finely powdered anhydrous aluminium chloride (5 grams), the gas is totally absorbed, and the sole products of the reaction are carbon tetrachloride and disulphur dichloride. Carbon chlorosulphide,  $\text{CSCl}_2$ , which is formed when carbon bisulphide is chlorinated in the presence of iodine, is not produced, and it appears that the whole of the bisulphide is converted

into the tetrachloride before any sulphur dichloride is formed. When a mixture of bromine and carbon bisulphide is heated with anhydrous aluminium chloride or bromide, carbon tetrabromide is formed, but the yield is small, and other reactions probably take place. N. L.

**Electrolysis of the Alkali Chlorides.** By F. WINTELER (*Zeit. Elektrochem.*, 1898, 5, 217—221. Compare F. Winteler, this vol., ii, 212, and F. Foerster, *ibid.*, 88).—Experiments on the electrolytic oxidation of sodium and potassium chlorates to perchlorates are described which confirm Foerster's results, and add a few details as to the effect of temperature and current density. T. E.

**Preparation of Pure Silver.** By OTTO PFEIFFER (*Chem. Zeit.*, 1898, 22, 775).—Pure silver may be prepared by dissolving silver residues in strong ammonia, distilling off the excess of ammonia, and precipitating the chloride with hydrochloric acid. The washed chloride is then placed in a porous cell with dilute sulphuric acid, the cell being surrounded by the dilute acid. A plate of amalgamated zinc, immersed in the external acid, is connected by a platinum wire with a piece of platinum foil, placed in the porous cell, and the apparatus left for one or two days; the reduced silver, after washing with water, is used for the preparation of pure silver nitrate. A. H.

**Preparation of Pure Silver.** By OTTO KUHN (*Chem. Zeit.*, 1898, 22, 868. Compare preceding abstract).—Well washed silver chloride obtained from silver residues, is placed in a platinum crucible which is immersed in very dilute sulphuric acid contained in a porcelain basin. A piece of zinc is placed in the basin, touching the external surface of the platinum crucible, and the reduction allowed to go on for about forty-eight hours. The finely divided silver is then boiled with dilute sulphuric acid, well washed, and used for the preparation of silver nitrate. A. H.

**Calcium Chloraluminat.** By GEORGES FRIEDEL (*Zeit. Kryst. Min.*, 1899, 31, 72—73; from *Bull. Soc. franç. Min.*, 1897, 20, 122—136).—Hexagonal-shaped tablets of the composition  $\text{AlO}_3\text{Ca}(\text{CaCl})\cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$ , and sp. gr. 1.892, are formed when a mixture of precipitated alumina, calcium chloride, and calcium oxide with water is heated at 400—500°. The crystals lose  $2\text{H}_2\text{O}$  at 105° without loss of transparency; this water can be regained from moist air; the remaining  $3\text{H}_2\text{O}$  is only expelled at a red heat, with decomposition of the salt. The hexagonal-shaped crystals consist of three monosymmetric individuals twinned together; at a temperature of 35°, all trace of twinning disappears, and the crystals are then optically uniaxial. As the temperature falls, or as the water is reabsorbed in a crystal which has been heated at 80—100°, there is a return to the original conditions. A slight pressure applied to the crystals brings about twinning, which again disappears when the pressure is taken off. L. J. S.

**Phosphorescent Strontium Sulphide.** By JOSÉ R. MOURELO (*Compt. rend.*, 1899, 128, 427—429).—The strontium sulphide, obtained from the carbonate by the action of sulphur vapour in absence of

oxygen, is white and non-phosphorescent when the carbonate is pure and free from alkalis and calcite, but with strontianite the product is deep grey and is highly phosphorescent. Other minerals containing strontium carbonate give less satisfactory results. Temperature has an important influence on the character of the product; if prepared at a dull or cherry-red heat, it is non-phosphorescent, and this holds good if prepared at a white heat, whilst a bright red heat gives the best result. The product obtained at too high a temperature does not become phosphorescent when re-heated (compare this vol., ii, 97 and 98.)

C. H. B.

**Yttria Earths contained in Monazite Sands.** By PAUL SCHÜTZENBERGER and O. BOUDOUARD (*Bull. Soc. Chim.*, 1898, [iii], 19, 227—236 and 236—244).—The author denotes by the term "yttria earths" those earths which yield double sulphates with potassium sulphate and dissolve in a saturated solution of the latter, but are precipitated by oxalic acid or ammonium oxalate; they were separated by precipitating the soluble double sulphates with hot potash, dissolving in nitric acid, precipitating by ammonia, repeating the last two processes several times to remove all trace of alkali, and finally dissolving in nitric acid and precipitating with oxalic acid. The oxides obtained by igniting the mixed oxalates were then dissolved in nitric acid and converted into sulphates, which were fractionally crystallised a large number of times; the fractions, on analysis, gave values for the atomic weight of the metal varying from 94—111, but no value could be obtained which remained constant after repeated crystallisation. Crystallisation of the sulphates, therefore, does not afford a means of separating a pure earth.

The pure yttria earths were then converted into the nitrates, which were fractionally decomposed to form the sub-nitrates by heating at 315—325°; the unchanged normal nitrate was removed from each fraction by dissolving in water, whilst the sub-nitrate fractions were converted into sulphates and analysed. Results for the atomic weight of the metal were obtained which varied from 93·0 to 162·5, although in neither direction was a limit attained. The higher fractions probably contained holmium, ytterbium, and erbium, whilst the lower values probably corresponded with yttrium; the latter element, however, appears to be present only in very small quantity in the monazite sands, although it is noteworthy that the spark-spectra of all the fractions corresponded with that of pure yttrium. W. A. D.

**Cæsium Manganese Alum.** By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1899, 20, 12—15).—*Cæsium manganese alum* is obtained according to the method already described by the author (*Abstr.*, 1898, ii, 521); the electrolysis of the mixed sulphates must be carried out at a temperature not exceeding 15°, and it is better to work at 0°. It crystallises in coral red, pentagonal hemihedric forms belonging to the cubic system, is decomposed by water and dilute acids with precipitation of manganese dioxide, gives a red solution in strong sulphuric acid (1 : 3), a yellowish-brown solution in concentrated nitric acid, and a brown solution in concentrated hydrochloric acid with evolution of chlorine; this solution becomes colourless on warm-

ing. The alum melts in its water of crystallisation at  $40^{\circ}$ , and cannot be dehydrated without decomposition. E. C. R.

**Fluoromanganites.** By RUDOLPH F. WEINLAND and O. LAUENSTEIN (*Zeit. anorg. Chem.*, 1899, 20, 40—45).—Potassium manganate dissolves to a violet solution in 40 per cent. hydrofluoric acid with evolution of heat, and on evaporation the solution yields a mixture of potassium permanganate and potassium fluoromanganite.

*Potassium fluoromanganite*,  $K_2MnF_6$ , obtained by dissolving potassium manganite (prepared by treating the manganate with water and carbonic anhydride) in hydrofluoric acid and potassium fluoride, crystallises in small, golden, transparent, hexagonal tablets [ $a:c = 1:1.6414$ ]. It turns reddish-brown when cautiously heated, and recovers its original colour on cooling; at a higher temperature, it volatilises, and in contact with moist air yields a violet residue, hydrogen fluoride being evolved, whilst at a strong heat it is decomposed into oxides of manganese and potassium fluoride. It is decomposed by water with precipitation of hydrated manganese peroxide, dissolves in cold hydrochloric acid to a dark brown solution which evolves chlorine when heated; when treated with cold concentrated sulphuric acid, it yields hydrofluoric acid, and with warm acid, oxygen and ozone. With nitric acid, it yields manganese bromide and hydrofluoric acid, and no manganese goes into solution; this reaction distinguishes it from Christensen's manganese trifluoride potassium fluoride (Abstr., 1887, 535). It yields a brownish-red solution with phosphoric acid, is insoluble in glacial acetic acid, oxidises oxalic acid in aqueous solution, decolorises indigo solution, and with hydrogen peroxide yields a reddish residue with evolution of oxygen.

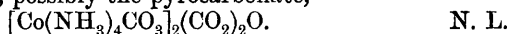
*Rubidium fluoromanganite*,  $Rb_2MnF_6$ , obtained by dissolving hydrated manganese peroxide in hydrofluoric acid and rubidium fluoride, crystallises in small, yellow, hexagonal tablets [ $a:c = 1:1.6185$ ], and resembles the potassium salt.

The above salts are the first crystalline halogen compounds of quadrivalent manganese which have been described, manganese tetrachloride being stable only in ethereal hydrochloric acid at low temperatures. They belong to the same type as potassium silicofluoride, potassium telluribromide, and potassium platinochloride. E. C. R.

**Absorption of Nitric Oxide by Ferrous Salts.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1898, [iii], 19, 343—347. Compare Abstr., 1897, ii, 145 and 262).—Determinations of the amount of nitric oxide absorbed at different temperatures by known weights of ferrous chloride, bromide and iodide dissolved in water and in alcohol, show that the absorption is not proportional to the amount of iron present in the solution, but depends rather on the nature of the salt, and, as has been previously shown, on the nature of the solvent. Thus, the amount of nitric oxide absorbed per 100 parts of iron is greater for the chloride than the bromide, and for the bromide than the iodide. In the case of the latter salt, the temperature seems to have but little influence on the absorption, either for aqueous or alcoholic solutions.

N. L.

**Preparation of Carbonatotetramminecobalt Hydrogen Carbonate.** By ARTURO MIOLATI (*Real. Accad. Linc.*, 1897, ii, 344—347).—In attempting to prepare carbonatotetramminecobalt thiocyanate by precipitating a solution of cobalt sulphate with the theoretical amount of barium thiocyanate and treating the filtered liquid according to Jörgensen's method, a red, crystalline salt was obtained, which analysis proved to be carbonatotetramminecobalt hydrogen carbonate. This production of the hydrogen carbonate, which Vortmann first obtained by saturating a solution of the normal carbonate with carbonic anhydride, is to be explained by its insolubility, as compared with the thiocyanate, under the experimental conditions. The author confirms Vortmann's description of the salt, but finds that, when heated at the temperature of the water-bath, it slowly decomposes and suffers a decrease in weight much greater than that corresponding with the loss of a molecule of water. Determinations of the electric conductivity of aqueous solutions gave the values  $\mu_{32} = 59.45$ ,  $\mu_{1024} = 79.18$ , and  $\mu_{\infty} = 82.6$ ; from these results, it is inferred that hydrolytic decomposition does not occur, and that the solution contains the salt of a dibasic acid with a univalent base, possibly the pyrocarbonate,



N. L.

**Action of Alkali Sulphites on Chromic Salts.** By ALBERT RECOURA (*Bull. Soc. Chim.*, 1898, 19, [iii], 168—170. Compare Abstr., 1895, ii, 501, 1896, ii, 27, 172).—When sodium sulphite (3 mols.) is added to a solution of chromium sulphate (1 mol.), the liquid changes in colour from violet to green, and contains sulphurous acid, sodium sulphate, and a basic chromium sulphite. The *basic sulphite*,  $2\text{Cr}_2\text{O}_3 \cdot \text{SO}_2$ , is completely precipitated on boiling the green solution. Another *basic sulphite*,  $\text{Cr}_2\text{O}_3 \cdot \text{SO}_2$ , obtained in a colloidal form on evaporating this solution on the water-bath, dissolves in water, forming a neutral solution which yields a precipitate after a time or on the addition of salts such as potassium chloride. Chromic hydroxide is not precipitated immediately on the addition of cold alkalis to the green solution; the addition of excess of sodium sulphite retards the precipitation, but does not altogether prevent it. Even in this case, a rise of temperature, or the addition of a considerable excess of ammonia, causes a deposition of the hydroxide from the unstable product of the combination of chromium sulphite and sodium sulphite.

G. T. M.

**Combination of Chromic and Titanic Acids.** By BLONDEL (*Bull. Soc. Chim.*, 1898, [iii], 19, 218).—Concentrated aqueous chromic acid dissolves titanic acid in different amounts depending on its concentration, temperature, and the method used in preparing the titanic acid; a concentrated solution containing 1 part of titanic oxide to 4 parts of chromic anhydride, when diluted with 8 parts of water at  $50^\circ$  or 6 parts of water at  $100^\circ$ , gives rise to a precipitate having the composition  $3\text{TiO}_2 \cdot 2\text{CrO}_3 + \text{H}_2\text{O}$ ; with 25 parts of cold water or 8 parts of water at  $100^\circ$ , the compound  $2\text{TiO}_2 \cdot \text{CrO}_3 + 2\text{H}_2\text{O}$  is formed, whilst dilution with 50 parts of cold water or 12 parts of water at  $100^\circ$  yields the compound  $3\text{TiO}_2 \cdot \text{CrO}_3 + 3\text{H}_2\text{O}$ . On adding ammonia (1 equiv.) to the same concentrated solution of the two oxides, the compound



$2\text{TiO}_2, \text{CrO}_3 + 2\text{H}_2\text{O}$  is precipitated, and, on evaporating the mother liquor in a vacuum, the compound  $\text{TiO}_2, 3\text{CrO}_3, (\text{NH}_4)_2\text{O} + \text{H}_2\text{O}$  separates in hexagonal prisms. W. A. D.

**Preparation of Pure Phosphotungstic Acid.** By ERNST WINTERSTEIN (*Chem. Zeit.*, 1898, 22, 539).—Pure phosphotungstic acid, free from alkali, is best prepared in the following manner. Sodium tungstate (4 kilos.) is dissolved in an equal weight of water and sodium phosphate (1 kilo.), dissolved in the boiling liquid. The solution is made slightly acid with sulphuric acid diluted with an equal volume of water, and evaporated until a crystalline crust forms, which disappears again on cooling. After some time, the syrupy liquid is poured off from the crystals of sodium sulphate, and extracted with ether, a small quantity of 70 per cent. sulphuric acid being added before each shaking. Heavy, oily, yellow drops of an ethereal solution of phosphotungstic acid collect at the bottom of the funnel and are removed, the extraction being continued until these no longer form. The ethereal extracts are united, water is added, and the whole extracted with fresh ether, the ether being distilled from the resulting solution in a current of steam. Chlorine is passed into the warm, dark coloured residue until it becomes light yellow, and, on cooling, the greater part of the phosphotungstic acid crystallises out, the remainder being obtained by evaporating the mother liquor. The yield amounts to about 2.3 kilos. with the quantities indicated. A. H.

**Action of Hydrofluoric Acid on Bismuthic Acid and Potassium Bismuthate.** By RUDOLPH F. WEINLAND and O. LAUENSTEIN (*Zeit. anorg. Chem.*, 1899, 20, 46—49).—When bismuthic acid is treated with 40 per cent. hydrofluoric acid at the ordinary temperature, a violent reaction takes place, and bismuth trifluoride is formed with evolution of oxygen and ozone. If, however, the reaction takes place at  $-10^\circ$ , a very unstable fluorine compound of quinquevalent bismuth is obtained, which cannot be isolated; the solution has strong oxidising properties, liberates iodine from potassium iodide, or chlorine from hydrochloric acid, converts alcohol into aldehyde, and rapidly destroys organic substances. With traces of manganese salts, the solution gives a violet-red coloration; when concentrated in a vacuum, it yields bismuth trifluoride, and when it is extracted with ether or poured into a large quantity of cold water, the theoretical quantity of bismuthic acid is precipitated. Potassium bismuthate behaves in a similar manner when treated with hydrofluoric acid. E. C. R.

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### Mineralogical Chemistry.

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**Inflammable Gas in Metalliferous Mines.** By GUSTAF NORDENSTRÖM (*Jahrb. f. Min.*, 1899, i, Ref. 262 ; from *Geol. För. Förh.*, 1896, 18, 637—640).—Inflammable gas issuing from borings in the metalliferous mines at Ämmeberg and Dannemora gave, on analysis by Särnström, the results under I and II respectively. The source of

the gas is unknown, but it has certainly not been derived by the decay of wood-work in water, as is sometimes the case.

	CH <sub>4</sub> .	C <sub>2</sub> H <sub>4</sub> .	CO <sub>2</sub> .	CO.	H.	N.	Total.
I.	51·0	0·5	1·5	1·2	1·0	44·8	100·0
II.	33·6	—	—	—	—	66·4	100·0

L. J. S.

**Strontianite from Bohemia.** By C. FRIEDRICH EICHLER (Verh. k.k. geol. Reichsanst., 1898, 297—298).—Analysis of strontianite from Lubna, near Rakonitz, gave

SrO.	CaO.	CO <sub>2</sub> .	Fe.	Total.	Sp. gr.
63·97	5·15	30·95	trace	100·07	3·703

It forms sheaf-like or columnar aggregates, which are pale yellow on the exterior, but white and translucent inside.

L. J. S.

**Chalybite and Vivianite in Dutch Peat.** By JACOBUS M. VAN BEMMELEN (*Jahrb. f. Min.*, 1899, i, Ref. 220; from *Archives Néerlandaises des Sci.*, Harlem, 1897, 30, 25—43. Compare this vol., ii, 302).—The peat of the moors in the south-east portion of the province of Drenthe, Holland, rests on alluvial sand and gravel cemented by siliceous and ferruginous material. The peat contains a relatively large amount of iron, with concretions and veins of white, amorphous chalybite, consisting of about 90 per cent. of FeCO<sub>3</sub>, and 10 per cent. of organic matter, with small amounts of phosphoric acid, magnesia and alkalis. Vivianite, in nodules of grey-blue or blue colour, is associated with the chalybite, or encrusts twigs and roots; it contains about 60 per cent. of Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and FeCO<sub>3</sub> in the proportion of 2:1, and about 40 per cent. of organic matter.

It is suggested that the iron has been collected as oxide by organisms, and afterwards converted into carbonate; part of the latter being then acted on by solutions of calcium and ammonium phosphate (from animal remains) to form the vivianite.

L. J. S.

**Minnesota Minerals.** By CHARLES P. BERKEY (*Jahrb. f. Min.*, 1899, i, Ref. 228—229; from *Ann. Rept. (1894) Geol. and Nat. Hist. Survey, Minnesota*, 1895, 23, 194—202).—The amygdaloidal diabase from Grand Marais, in the Lake Superior district, contains in the cavities, laumontite and strigovite with some quartz. The decomposed rock gave analysis I. Apophyllite crystals (anal. II; also trace of fluorine) are often intergrown with laumontite, to which is probably due the alumina shown in the analysis; sp. gr. 2·34. Laumontite (anal. III) occurs as fine needles. Strigovite (anal. IV) forms a thin coating on the walls of several of the amygdulæ.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	55·40	22·55	14·67	3·75	1·41	0·74	—	—	0·97	99·49
II.	52·61	0·67	trace	—	25·22	0·17	3·03	1·71	16·17	99·58
III.	53·87	18·06	0·88	—	11·19	0·45	0·29	0·67	13·18	98·59
IV.	33·14	13·22	24·20	12·19	1·50	3·49	—	—	12·34	100·08

Datolite occurs at Flood Bay, on Lake Superior, in snow-white, compact masses, with a very finely crystalline structure. H, 4½; sp. gr., 2·9. Analysis gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	B <sub>2</sub> O <sub>3</sub> .	Total.
36·90	1·51	35·67	5·60	[20·32]	100·00

Analyses are also given of travertine and calcareous marl.

L. J. S.

**Asbestos Deposits of Val Malenco.** By LUIGI BRUGNATELLI (*Jahrb. f. Min.*, 1899, i, Ref. 211 ; from *Rend. R. Ist. Lombardo*, 1897, [ii], 30, 1109—1119).—Minerals from the large deposits of asbestos in the Val Malenco, Lombardy, are described. The asbestos in fine white fibres is the chrysotile variety of serpentine.

A magnesium carbonate is found in compact, snow-white masses, which, under the microscope, is optically biaxial and apparently orthorhombic. Analysis gave :—

MgO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
43·32	21·85	34·32	99·49	2·001—2·025

This may be identical with the Vesuvian hydrogiobertite, or it may be a new mineral.

Crystallographic descriptions are given of magnesite, dolomite, aragonite, and magnetite ; the last contains some titanium.

L. J. S.

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## Physiological Chemistry.

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**Fate of Carbonic Oxide in the Animal Body.** By F. WACHHOLTZ (*Pflüger's Archiv*, 1899, 74, 174—180).—The chief result of the experiments recorded is that the main portion of the carbonic oxide inspired is destroyed in the tissues, being converted into carbonic anhydride. Only so much is expired as such as can be explained by the relative tensions of the carbonic oxide combined as carboxy-hæmoglobin, and that in the alveolar air. W. D. H.

**Influence of Sodium Chloride on Proteid Metabolism.** By WALTHER STRAUB (*Zeit. Biol.*, 1899, 37, 527—549).—Seven experiments are recorded; they were made on dogs which were given a fixed diet, to which, on some days in the course of the observations, a certain quantity of sodium chloride was added. With small doses (3 grams), there was no effect on proteid metabolism; in one case, there was some diuresis. Even with larger doses (12 to 20 grams), the effect is a small one; there was certainly no marked increase of proteid metabolism, as some older observers stated. The first effect of these larger doses is a fall, followed by a rise, of proteid katabolism. This is mainly attributed to the salt's power of attracting water. W. D. H.

**Alterations of Concentration by the Diffusion of Two Substances in Solution into one another. Absorption in the Small Intestine.** By RUDOLF HÖBER (*Pflüger's Archiv*, 1899, 74, 225—245, 246—271. Compare Abstr., 1898, ii, 298).—The first of these two papers deals with the physical problems indicated by the

title, and the second with the application of these principles to the elucidation of the subject of absorption. The general conclusion drawn is that in the absorption of salts there is no necessity to regard the process as due to the 'vital' action of cells; the diffusibility of salts determines their capacity for absorption. W. D. H.

**Influence of Choline on the Circulation.** By LÉON ASHER and HORATIO C. WOOD, jun. (*Zeit. Biol.*, 1899, 37, 307—319).—In experiments made on dogs and rabbits, doses of 3 to 10 c.c. of a 5 per cent. solution of choline were injected intravenously; the main effects of these large doses are (1) a cessation of respiration, (2) an elevation of arterial pressure. These effects are considered to be due to the action of the base on the respiratory and vaso-motor centres respectively. W. D. H.

**Absorption and Excretion of Iron in the Guinea-pig.** By G. SWIRSKI (*Pflüger's Archiv*, 1899, 74, 466—510).—The research is mainly histological, and deals with the kind of cells chiefly concerned in the absorption of iron in the guinea-pig. The iron reaction is obtained in the whole length of the alimentary canal with the exception of the stomach. In the duodenum, the iron-containing substance is in the form of fine granules, but this is not regarded as sufficient evidence that the duodenum is the only place where absorption of iron administered either in the food or in the form of drugs is absorbed, although that view is taken by some previous observers.

The iron reaction can be traced through the epithelium, the adenoid tissue beneath it and its cells, and the blood vessels. Certain forms of leucocytes which appear to be specially concerned in the process are designated "Fe-cytes."

In relation to the excretion of iron, the principal new point of interest raised is the possibility of excretion through the respiratory mucous membrane. W. D. H.

**Urea in the Animal Organism, and in Normal Mammalian Muscle. Urea in various Animal Fluids. Formation of Urea in the Liver.** By BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1899, 74, 307—356; 357—360; 361—363).—The main bulk of the first of this series of papers is devoted to a review of previous work on the subject; the last is polemical, and is directed against Salaskin, who has failed to find urea in mammalian muscle. The main point insisted on throughout is that urea is present in by no means insignificant amount in muscular tissue. The principal conclusions from the author's own experiments are the following:—

1. The various tissues investigated gave the following average results:

Blood contains.....	0·1157	per cent. of urea.
Muscle „ .....	0·0884	„ „
Liver „ .....	0·1115	„ „
Kidney „ .....	0·6695	„ „
Heart „ .....	0·1734	„ „
Spleen „ .....	0·1215	„ „
Pancreas „ .....	0·1189	„ „
Brain „ .....	0·1280	„ „

2. Bird's blood (goose) contains 0.0174 per cent. of urea. In mammalia, the amount rises with the amount of proteid in the food; the percentage in the blood of the pig, man on mixed diet, and dog on flesh diet are respectively 0.0284, 0.0611, and 0.120.

3. The amount of urea in human milk and human amniotic fluid is about the same as in the blood. The amount of proteid in human milk is given as 1.409 per cent.

4. Of the nitrogen contained in substances not precipitated by a mixture of phosphotungstic and hydrochloric acids, about 38 per cent. in goose's blood, and 50–60 per cent. in the animal fluids investigated, is present as urea.

W. D. H.

**Action of Superheated Water on Proteids.** By ERNST SAL-KOWSKI (*Zeit. Biol.*, 1899, 37, 404–416. Compare Abstr., 1898, ii, 173).—Polemical. A reply to Neumeister's criticisms (*Zeit. Biol.*, 36, 420).

W. D. H.

**Chlorophyll in the Livers of Invertebratæ.** By A. DASTRE and N. FLORESCO (*Compt. rend.*, 1899, 128, 398–400).—When the dried and powdered livers of molluscs and other animals which are supposed to contain chlorophyll or xanthophyll are treated with chloroform, hæmochromogen remains undissolved, and the solution contains only hepatochlorophyll or hepatoxanthophyll, together with cholechrome, and the latter shows no absorption bands. The solution shows bands at  $\lambda 670$ – $646$ ,  $\lambda 548$ – $530$ ,  $\lambda 520$ – $507$ , and  $\lambda 611$ – $596$ ; the first being the most distinct, and the last the weakest. The band at  $524$ – $507$  is sometimes missing, even when the band at  $611$ – $596$  is visible.

It is noteworthy that the three bands  $670$ – $646$ ,  $611$ – $596$ , and  $548$ – $530$  coincide with the bands I, II, and IV, of Tschirch's xanthophyll, and it follows that hepatoxanthophyll is identical with that of vegetable origin.

Direct experiments in which edible snails were kept for some time on a diet containing no chlorophyll showed that, under these conditions, the hepatochlorophyll disappeared, but reappeared when chlorophyllic substances were added to the diet. This fact, and the irregular occurrence of the hepatochlorophyll, show that it is really of vegetable origin, derived from the vegetable food of the particular animal, and is absorbed and tenaciously retained by the hepatic tissues.

C. H. B.

**Reducing Power of the Tissues: Liver and Pancreas.** By HENRI HÉLIER (*Compt. rend.*, 1899, 128, 319–322).—The author measures the reducing power by boiling 5 grams of the fresh tissue with water for an hour, filtering, and diluting to 100 c.c.; 10 c.c. of the solution are then left for 24 hours with 25 c.c. of  $N/10$  potassium permanganate, and, after filtering, are mixed with an excess of aqueous sulphurous acid containing a small quantity of sulphuric acid, and the excess finally estimated by means of very dilute permanganate solution. Whilst the reducing values so obtained are practically constant for the tissue of a dog's heart, they vary in a marked manner in the case of the liver and pancreas. Immediately after a meal, a high reducing value of the liver is observed, which gradually diminishes to less than one-half

after 3 hours; a rapid increase then occurs, until after 10 hours it attains a maximum value greater than that first observed. In the case of the pancreas, similar results are obtained, but they are not so well defined. The influence of habit on the reducing power of the tissue is remarkable; when a guinea pig is fed 3 hours after its ordinary time and then killed 3 hours later, the reducing power of both liver and pancreas corresponds with that of the *sixth* hour under the ordinary conditions of feeding. The importance of considering this "functional memory" (*mémoire cellulaire*) in physiological research is thus emphasised.

W. A. D.

**Sulphur in the Urine under Various Conditions.** By ERICH HABNACK and FRIEDRICH K. KLEINE (*Zeit. Biol.*, 1899, 37, 417—442).—The experiments recorded are considered to show that the estimation of sulphur in the urine gives a valuable indication of changes in the metabolic processes in the organism. The first series of experiments were performed on dogs; in their urine, sulphur is combined (*a*) as ordinary sulphates, (*b*) as ethereal sulphates, (*c*) as thiosulphates, and (*d*) as organic sulphur compounds. Dogs are very profoundly affected by chloral hydrate, and often small doses are fatal. The main effect on the sulphur in the urine is an increase of the 'neutral sulphur,' at the cost of the other sulphur-containing constituents of the urine.

In order to investigate the effects of alkalis, two grams of sodium carbonate were given daily with the food. This led to an increased combustion in the body, a marked decrease in the 'neutral' sulphur, and a corresponding increase of oxidised sulphur; there was also no storage of sodium compounds in the body. Small doses of soda abolish the action of chloral hydrate just described. Numerous observations on human beings in various pathological states are appended, but no general conclusions are drawn from these.

W. D. H.

**The Sugar in Diabetic Urine.** By GUSTAVE PATEIN and E. DUFAU (*Compt. rend.*, 1899, 128, 375—377).—Various conflicting statements have been made as to the nature of the sugar in diabetic urine, and it is known that such urine may cease to contain glucose and then become lævogyrate. The author has endeavoured to throw light on these points by precipitating the proteids with an acid solution of mercuric nitrate followed by an excess of sodium hydroxide instead of with basic lead acetate. The sugar in the liquid was then estimated by means of the polarimeter, and also by Fehling's solution. Even when the polarimeter gives higher results than Fehling's solution, the sugar present is dextrose (*d*-glucose); when there is a difference between the results obtained by the two methods, it is due to the presence in the urine of lævogyrate compounds that are precipitated by mercuric nitrate in acid solution, but not by basic lead acetate.

C. H. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Fermentation of Saccharides.** By ELISÉE DUBOURG (*Compt. rend.*, 1899, 128, 440—442).—Certain yeasts, when added to a solution of saccharose, produce no fermentation, but if they are added to a solution containing a high proportion of nitrogenous matter (for instance, 25 per cent. of an infusion of yeast), together with 5 per cent. of glucose and 5 per cent. of saccharose, the glucose and the greater part of the saccharose quickly disappear, and any sugar remaining is completely inverted. With less than 0.5 per cent. of glucose, however, this only disappears, and the saccharose is not attacked; with 1.5 to 2 per cent. both sugars are affected.

Under similar conditions and with suitable yeasts, even the sugars difficult to ferment, such as galactose, behave in the same way, but lactose always offers resistance. The results seem to be due to the production of a much larger quantity of the ferment in the highly nitrogenous liquid. If, after fermentation, the liquid is decanted, the residue is washed with sterilised water until free from sugars and a nutritive solution of saccharose is poured over it, the sugar is soon completely inverted and begins to ferment.

With moulds, on the other hand, under similar conditions, only those sugars are attacked that would be similarly affected by simple inoculation; lactose, raffinose, and saccharose do not ferment. It is noteworthy that the only two saccharides which are attacked by moulds, trehalose and maltose, yield glucose only when hydrolysed, and in this respect are analogous to starch, which is the only member of its group that will ferment with *Mucorinae*.  
C. H. B.

**Chemical Action of Pathogenic Micro-organisms.** By LOUIS HUGOUNEQ and M. DOYON (*Ann. Chim. Phys.*, 1898, [vii], 145—156).—The action of pathogenic micro-organisms in promoting fermentation is observed by adding cultures to sterilised glucose solutions containing nutrient materials placed in contact with excess of calcium carbonate and maintained at 35° for a definite length of time. At the close of the experiment, the unaltered glucose is determined in one portion of the solution, the remainder is filtered, the precipitate examined for succinic acid, and the filtrate, acidified with oxalic acid, is distilled to remove alcohol and volatile acids. The final mother liquor is evaporated nearly to dryness, extracted with ether, and the extract examined for lactic acid.

*Staphylococcus aureus* produces small quantities of alcohol and inactive lactic acid; the gas evolved consists of carbonic anhydride and hydrogen; the greater part of the glucose remains unchanged.

*Bacillus coli communis* gives rise to both inactive and dextro-rotatory lactic acids, ethylic alcohol, and a volatile acid not identified. An anærobic culture of the bacillus causes an evolution of hydrogen and carbonic anhydride. A similar result is obtained with the tetanus bacillus, whilst the latter gas and nitrogen are evolved in the case of Eberth's bacillus.

*Streptococcus pyogenes* and the cholera bacillus have little or no fermentative action.

Under favourable conditions, Eberth's bacillus and *B. coli communis* (compare Abstr., 1897, ii, 114) decompose the alkaline nitrates in 1½ per cent. solutions, setting free nitrogen and the corresponding alkali, and utilising the oxygen.

Biliverdin added to a nutrient solution containing *Staphylococcus aureus*, the septic vibrio, the cholera bacillus, Eberth's bacillus, or *B. coli communis*, is decomposed with the formation of a red colouring matter. Bilirubin under these conditions also undergoes decomposition, yielding the same product. The new colouring matter, unlike bilirubin and its derivatives, is soluble in water, and its solution is dichroic. Hæmoglobin is converted into hæmatin by the action of these organisms.

Outchinsky maintains that certain micro-organisms, cultivated in nutrient solutions containing no proteids, bring about the formation of active substances resembling albumin. The author, employing the solution recommended by this investigator, obtains negative results in the case of Löffler's bacillus and the bacilli of cholera and diphtheria.

G. T. M.

**Production of Aromatic Substances by Alcoholic Fermentation in Presence of certain Leaves.** By GEORGES JACQUEMIN (*Compt. rend.*, 1899, 128, 369—371).—When the must of grapes is mixed with an aqueous extract of leaves from the same vine and then allowed to ferment, the wine obtained is superior in flavour and bouquet to wine obtained from the same must in the ordinary way. This result is due partly to the formation of aromatic compounds from the substances derived from the leaves (Abstr., 1898, ii, 397), and partly to the fact that the glucosides, &c., in the extract of the leaves promote the development of the most beneficial yeasts. The addition of the leaves themselves, instead of the extract, to the must does not give satisfactory results.

C. H. B.

**Presence of Hydrocyanic Acid in Various Plants.** By ALEXANDRE HÉBERT (*Bull. Soc. Chim.*, 1898, [iii], 19, 310—313).—A number of plants, the reputed toxic properties of which have been attributed to the presence of hydrocyanic acid, were examined, having regard to the existence of the acid both in the free, or feebly combined, state and in the form of glucosides analogous to amygdalin.

*Aroideæ*.—No hydrocyanic acid was detected in *Arum maculatum*, *Arum Italicum*, *Arisarum vulgare*, *Amorphophallus rivieri*, *Caladium bulbosum*, and *Diffenbrachia seguine*.

*Saxifrageæ*.—Hydrocyanic acid, in the free, or feebly combined, state, was found in the young, green shoots of *Ribes rubrum*, to the extent of a few milligrams per 100 grams; only traces are contained in the full-grown green parts of the plant. Smaller amounts of hydrocyanic acid occur in *R. nigrum* and *R. aureum*, but none was detected in *R. sanguineum* and *R. uva crispa*.

*Rosaceæ*.—Hydrocyanic acid is not contained in the cultivated

varieties of *Rosa*. The embryo of the fruit of *Eryobothrya Japonica* yields about 0.04 per cent. of the acid, which results from the hydrolysis of a glucoside by a soluble ferment; it is not found in the pericarp or the seminal integument.

*Ranunculaceæ*.—The leaves, stalks, and buds of *Aquilegia vulgaris*, at the commencement of vegetation, yielded, per 100 grams, 1.2, 3.6, and 10.0 milligrams respectively of hydrocyanic acid, formed by the hydrolysis of a glucoside by a soluble ferment. The expanded flowers contain a much smaller quantity of the acid, which exists in the free, or feebly combined, state, and almost entirely in the ovaries (0.01 per cent.).

In none of the plants examined is there sufficient hydrocyanic acid to constitute a means of defence, or to produce serious toxic effects in ordinary circumstances. The fact that the acid occurs only in the chlorophyllaceous parts of *Aquilegia vulgaris* seems to confirm Gautier's views on the formation of proteids in plants. N. L.

**Manurial Value of Oil Cakes.** By L. MALPEAUX (*Ann. Agron.*, 1899, 25, 111—126. Compare Abstr., 1897, ii, 383).—Field experiments were continued on the same lines as those previously described, and were supplemented by pot experiments with each manure. The results indicate that the different cakes act very differently; sesamé, as before, proved to be the best, whilst the values of the others decrease in the order: poppy, earth-nut, camelina, colza, castor-oil, cotton, and palm.

For spring sowing, cakes which act rapidly, such as poppy-seed, sesame, and castor-oil, should be employed, and they should be applied as early as possible. These cakes and camelina act more quickly than the others, which should be reserved for late crops.

The classification, as indicated by the author's experiments, is not absolute, and might have to be altered under different conditions of soil and season. N. H. J. M.

**Action of Organic Nitrogen, especially in Farmyard Manure.** By THEODOR PFEIFFER, E. FRANKE, OTTO LEMMERMANN, and H. SCHILLBACH (*Landw. Versuchs-Stat.*, 1899, 51, 249—310).—The following results were obtained from two series of experiments, made in pots and on small plots, extending over three years.

Horn meal, blood meal, and dung gave, in the pot experiments, far better results than those obtained by Wagner, the values of the nitrogen (compared with nitrate = 100) being: horn meal, 83—84; blood meal, 85; and dung, 49, as against 63, 69, and 32 (Wagner). The after effect of the manures was very considerable.

One lot of farmyard manure which, in the pot experiments, gave the value 46, gave in two plot experiments the values 92 and 93 (nitric nitrogen = 100). The manure decomposes more quickly in soil under natural conditions than in pots, owing to the increased circulation of water and the resulting drying up of the surface.

In light, sandy soil (plots), the dung was effective with mustard in the second year, but not in the third year. In the case of the heavy soil at Rothamsted, the effect of farmyard manure is clearly visible after 23 years. This difference is attributed to the

different rates of decomposition depending on aeration, and for this reason, results obtained with farmyard manure must be considered in conjunction with soil conditions.

Since the nitrogen of the dung applied to plots was utilised to an extent almost equal to nitrogen as nitrate, the manure cannot have caused denitrification to any extent, notwithstanding that in one case as much as 600 cwt. was applied per hectare.

In the case of the pot experiments, it is possible that, owing to imperfect aeration, there was a considerable loss of nitrogen in the free state, but it is doubtful whether such loss could have been great enough to account for the unsatisfactory results obtained.

N. H. J. M.

**Field Experiments on the Effect of the Phosphoric Acid of Basic Slag and Bone Meal.** By EMERICH MEISSL and OTTO REITMAIR (*Zeits. Landw. Versuchswesen Oesterr.*, 1898, 1, 6—77).—The crops selected for the experiments were winter wheat and rye. The manures employed had the following percentage composition :

		Fine meal.	Total $P_2O_5$ .	Solubility in citrate.
Basic slag	I.....	82.4	18.03	93.5
"	II.....	87.0	18.16	50.6
Bone meal	.....	77.5	30.11	71.2

With regard to the effect produced by the two lots of basic slag, the results indicated that the phosphoric acid was equally valuable, both as regards the amount and the quality of the produce, notwithstanding the great difference in solubility in citrate. The general effect was to improve the relation of grain to straw, as compared with the unmanured plot; the percentage amount of phosphoric acid in the produce was not appreciably altered by the manure.

So far as autumn manuring is concerned—no spring manuring results are as yet available—the solubility of basic slag in citrate can no longer be considered as a criterion of the value of the manure. The older method of valuation, according to the amounts of fine meal and total phosphoric acid, seems to be the most satisfactory. At the same time, the citrate method is valuable in detecting adulteration with mineral phosphates. (Compare Dafert and Reitmaier, this vol., ii, 382).

In comparison with basic slag, degelatinised bone meal gave, on the whole, better results as regards amount of produce, and equally good results as regards the quality of the crop.

N. H. J. M.

### Analytical Chemistry.

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Measuring the Volumes of Liquids: Preparation of Normal Solutions. By JULIUS WAGNER (*Zeit. physikal. Chem.*, 1899, **29**, 193—219).—The accuracy attainable in ordinary volumetric work and the probable errors resulting in the use of pipettes, burettes, and

measuring flasks are discussed. The various methods of emptying pipettes were tested and all found capable of giving results accurate to 0.05 per cent., if care was taken to keep the time of outflow sufficiently great, practically no difference was found in the volume of different solutions delivered by a pipette. Measuring flasks can be used with a very high degree of accuracy if care is taken to dry the neck above the mark. All burettes require careful calibration, after which, for quantities above 20 c.c., the values are probably accurate to 0.05 per cent. Errors due to temperature variations are important; thus a change from 15° to 25°, if uncorrected, leads to errors of 0.2 to 0.3 per cent.; a table of temperature corrections is given. Examples are finally given to indicate the untrustworthiness of the commercial guarantee of purity of reagents. L. M. J.

**Protection of Standard Solutions.** By WILHELM STEINFELS (*Zeit. anal. Chem.*, 1899, 38, 154—165).—When standard solutions which undergo alteration on exposure to atmospheric air (alkali hydroxides, stannous chloride) are stored in tubulated reservoirs from which the burettes are filled by opening a stopcock, they require to be protected by admitting the air through an appropriately charged U-tube. The author has devised a form of glass stopcock, and also an arrangement of caoutchouc tubes with a special pinch-clamp, by either of which the connection of the U-tube both with the reservoir and with the external air is opened and closed by the action which draws out the solution. The absorption of moisture from the solution and the deterioration of the protecting substance are thus almost completely prevented. Figures of the apparatus are given.

M. J. S.

**Estimation of Fluorine and Carbonic Anhydride, and the Estimation of Fluorine in Teeth.** By WALTHER HEMPEL and W. SCHEFFLER (*Zeit. anorg. Chem.*, 1899, 20, 1—11).—The sample for analysis is mixed with finely-powdered quartz in the ratio of 15 parts to 1 part of fluorine, and treated with concentrated sulphuric acid under diminished pressure in a flask which is connected with a gas burette. Great care must be taken to ensure the absence of moisture from the apparatus. The mixture of silicon fluoride, carbonic anhydride, and other gases is measured and treated with water, to decompose the silicon fluoride, and the residual gas is again measured; the difference in the volume gives the volume of silicon fluoride. The carbonic anhydride is then estimated in the residual gas by absorption in potassium hydroxide, and the small quantity of carbonic anhydride which is absorbed during the treatment with water is collected by washing it out of the water by a stream of the residual gas from which the main quantity of the carbonic anhydride has been absorbed. The results are accurate, and an estimation of the fluorine can be performed in about 2 hours. A full description, with drawings of the apparatus, is given in the original paper.

Before estimating the fluorine in teeth, it is necessary to completely destroy all organic matter, since, in the subsequent treatment with sulphuric acid, it would cause the formation of sulphurous anhydride. This is easily effected by burning the finely-powdered teeth in a

current of oxygen and no loss of fluorine takes place, provided that the pulverised teeth are in a very thin layer. The analysis of human teeth gave, for sound teeth, 0.33 and 0.52 per cent., and for unsound teeth, 0.19 per cent. of fluorine in the ash. E. C. R.

**Estimation of Dissolved Oxygen in Water.** By ALBERT LÉVY and FÉLIX MARBOUTIN (*Bull. Soc. Chim.*, 1898, [iii], 19, 149—151. Compare Abstr., 1897, ii, 430).—The method for the estimation of dissolved oxygen in water, previously described by one of the authors, having been adversely criticised by Sokoloff, and also by Klopine, fresh experimental results are brought forward in support of the accuracy of the process, and it is pointed out that the objections raised against it are founded partly on mistranslations and partly on ignorance of various papers published in the *Annuaire de l'observatoire municipal de Montsouris*, more especially that of 1894. N. L.

**Table for Calculation of Analyses of Fuming Sulphuric Acid.** By LEO GRÜNHUT (*Zeit. anal. Chem.*, 1899, 38, 167—171).—The results of acidimetric titration are expressed as  $H_2SO_4$ , and a reference to the table gives at once the percentage of sulphuric anhydride present.

M. J. S.

**Estimation of Nitrogen by Kjeldahl's Method.** By LÉON MAQUENNE and E. ROUX (*Ann. Agron.*, 1899, 25, 76—82).—In digesting the substance to be analysed with sulphuric acid, mercury, and potassium sulphate, it is necessary to continue the heating for half-an-hour after the liquid has become colourless, otherwise low results are obtained.

Addition of zinc before distilling is to be avoided, owing to the readiness with which nitrates are reduced to ammonia; pumice must only be used after it has been ignited and powdered. Check experiments should be made with all the reagents employed; as much as 3.65 milligrams of nitrogen as ammonia has been found in 20 c.c. of pure sulphuric acid. When caustic soda containing much carbonate is employed, there may even be (in check experiments) an increase in acidity, and to avoid this source of error it is proposed to insert a cup of wire gauze containing pumice in the neck of the distilling flask (which may be contracted at the base); when the alkali is poured into the flask, the pumice becomes saturated with it, and so retains any carbonic anhydride given off during the distillation.

The use of sodium sulphide for liberating ammonia from its compounds with mercury is objectionable as sometimes interfering with the titration; its action is, moreover, incomplete. Instead of it, the author employs sodium hypophosphite, a gram of which is measured in the dry state, in a spoon, dissolved in 20 c.c. of water, and added to the diluted, still acid solution. The reduction of the mercury salt is very rapid when the liquid is heated, a few minutes at 70—80° being sufficient. When cold, powdered pumice and alkali are added, and the analysis completed in the usual manner.

There is no object in continuing the distillation for more than half-an-hour; in this time, the distillate amounts to about 45 c.c. Results of several analyses are given, showing that somewhat higher results

are obtained when sodium hypophosphite is employed than with the sulphide.  
N. H. J. M.

**Simple Addition to the Apparatus for Kjeldahl Nitrogen Estimations.** By FRITZ PREGL (*Zeit. anal. Chem.*, 1899, 38, 166—167).—The object of this addition is to prevent regurgitation of the standard sulphuric acid in the absorption flask in case of any accidental diminution of pressure in the distillation flask. A simple trap, consisting of a small glass bulb with a tubular neck continued internally nearly to the bottom of the bulb, and plunging to a depth of about 2 mm. into mercury in the bulb, is passed through the caoutchouc stopper of the distillation flask. There is a hole in the side of the bulb near the top. Should diminution of pressure occur, air enters through the trap, but the mercury prevents any escape in the opposite direction. When this trap is used, the distillation requires no attention whatever.  
M. J. S.

**Reactions for the Detection of the Nitro-group.** By S. P. MULLIKEN and E. R. BARKER (*Amer. Chem. J.*, 1899, 21, 271—276).—All nitro-compounds, when dissolved in dilute alcohol containing traces of some neutral salt, such as calcium chloride, are readily reduced by zinc dust to hydroxylamino-derivatives (compare Bamberger, *Abstr.*, 1894, i, 373; and Wöhl, *ibid.*, 409). As a qualitative test, the reaction is best applied by dissolving 3 or 4 drops of the nitro-compound in 3 c.c. of 50 per cent. alcohol, adding 5 or 6 drops of a 10 per cent. calcium chloride solution, and then heating until violent boiling begins; the mixture is then left for 2—5 minutes, filtered, and the filtrate tested with ammoniacal silver nitrate, the presence of a nitro-compound being shown by the strong reducing power of the solution. Nitroso-, azo-, and azoxy-derivatives give the reaction.

Nitrobenzene, in the presence of a little iron and hydrochloric acid, acts as an oxidising agent in the conversion of "aniline-red oil" (a mixture in equal parts of aniline, and ortho- and para-toluidines) into rosaniline, and, as Lange showed (*Abstr.*, 1885, 1130), any other nitro-compound may be substituted for nitrobenzene in the reaction. Three or four drops of the nitro-compound are boiled for 2—3 minutes in a test-tube with 2 c.c. of "aniline-red oil," 2 c.c. of distilled water, 2 c.c. of concentrated hydrochloric acid of sp. gr. 1.20, and 1 gram of iron filings, an excess of acid being carefully avoided, as it prevents the appearance of the colour. The red colour of the rosaniline is best observed by pouring a few drops of the dark-coloured liquid into dilute acetic acid. The "aniline-red oil" used should be nearly colourless. The coloration is not very marked with di- or tri-nitro-compounds. In addition to nitro-compounds, any substance containing oxygen directly attached to nitrogen, as, for example, azoxybenzene, nitrosobenzene, methylphenylnitrosamine, acetoxime, and ethylic nitrite or nitrate, gives the reaction.  
J. J. S.

**Valuation of Basic Slag.** By FRANZ W. DAFERT and OTTO REITMAIR (reprinted from *Zeits. Landw. Versuchswesen Oesterr.*, 1899, 2, pp. 25).—Whilst the results of Meissl and Reitmair's experiments



(this vol., ii, 379) indicated that it is wrong to value basic slag according to the solubility in citrate rather than according to the total phosphoric acid, subsequent experiments made in pots (Reitmair, *Zeits. Landw. Versuchsw. Oesterr.*, 1899, 2, 24) showed a relatively good agreement between the amount of phosphoric acid taken up and the solubility in citrate or citric acid. Without underrating the importance of these results, which accord with those obtained by Wagner, it is pointed out that, in practice, increased yield of corn and straw is what is wanted. From this point of view, it is maintained that the results of these and of Wagner's experiments indicate that it is, as a rule, the amount of total phosphoric acid in basic slag on which the yield of corn and straw depends, whilst the completeness and rapidity of the action depend on the fineness and on the chemical nature of the slag. The solubility of the phosphoric acid in dilute acids gives, within certain limits, very useful indications as to the value of the slag; but Wagner's citrate solubility method is not, *per se*, entirely trustworthy as a means of ascertaining the practical value of the manure.

After trying a number of solvents, it was found that a 5 per cent. solution of formic acid furnished results which agreed best with the production of corn. It is therefore proposed that basic slag should be valued according to the total phosphoric acid when 90 per cent. of the total is soluble in 5 per cent. formic acid.

*Estimation of Total Phosphoric Acid.*—Ten grams of the slag are boiled for 15 minutes with 100 c.c. of nitric acid of sp. gr. 1.4 in a half-litre flask; water (300 c.c.) is then added, and the solution, after cooling, is diluted to 500 c.c. Of the filtered solution, 25 c.c. are mixed with 20 c.c. of nitric acid in a beaker, without using a rod, and, while lukewarm, 75 c.c. of a concentrated molybdate solution are quickly added. After 5 minutes, the mixture is stirred violently for a whole minute. In about half-an-hour it is filtered, washed with a mixture of the concentrated molybdate solution (1 part) and water (20 parts), dissolved in 2.5 per cent. ammonia, and precipitated with magnesia mixture.

The molybdate solution is prepared as follows:—Powdered ammonium molybdate (400 grams) is dissolved in hot water (about 650 c.c.), diluted to 1000 c.c., and after quickly cooling to 20°, again made up to a litre. Ammonium nitrate (200 grams, previously weighed) is then added to 870 c.c. of nitric acid (sp. gr. 1.300 at 15°), stirred violently until the temperature falls to about 10°, and the whole immediately poured, in a thin stream, into the molybdate solution, which is violently stirred all the time. After being kept for 48 hours at 20–30° in a good light, the solution is filtered, and kept in a cool, dark place.

The magnesia mixture is a solution of crystallised magnesium chloride (55 grams) and ammonium chloride (70 grams) in 1 litre of 2.5 per cent. ammonia.

*Estimation of Phosphoric Acid Soluble in Formic Acid.*—Five grams of the slag, in a 500 c.c. flask, are moistened with alcohol (5 c.c.), the flask filled to the mark with 5 per cent. formic acid, and rotated for 30 minutes in a Wagner apparatus; 75 c.c. of the filtered extract are

poured into a pear-shaped vessel terminating in a cylinder with 0.1 c.c. divisions, and treated with 75 c.c. of the molybdate solution. The cylinder is closed, kept upright for 5 minutes, and shaken upside down as violently as possible for half a minute. After a few minutes, when most of the precipitate has deposited in the cylinder, any portions of the precipitate adhering to the cork are washed down into the liquid, and the whole kept upright for 2 hours; it is then shaken in the machine for 15 minutes, allowed to settle for an hour, and the volume of the precipitate read off. The number of c.c., multiplied by a factor to be determined, gives with sufficient accuracy the amount of phosphoric acid dissolved.

The factor is obtained by determining gravimetrically the amount of soluble phosphoric acid in a number of samples for which the above method has been employed. The results of actual determinations, being divided by the corresponding volumes of precipitates, yield an average value which is taken as the factor. The factor does not depend on the process if carried out exactly as described, but does depend, to some extent, on the form of the pear-shaped vessel. The method is applicable to any extracts of slags.

N. H. J. M.

**Estimation of Carbonic Oxide.** By CHARLES FRÉDÉRIC SCHLAGDENHAUFFEN and PAGEL (*Compt. rend.*, 1899, 128, 309—311).—When carbonic oxide is slowly passed over carefully dried silver oxide at 60°, it is completely converted into carbonic anhydride, and the method can be employed for its estimation. Dry cuprous oxide is not acted on by carbonic oxide at 100°, but at higher temperatures is reduced to metallic copper, the conversion of carbonic oxide to anhydride being complete at 300°. Dry bismuth oxide remains unaltered in presence of carbonic oxide at temperatures below 230°, but at 400° it is reduced to the lower oxide without yielding the metal; red lead commences to undergo change at 225°, whilst litharge is only acted on at temperatures above 300°, metallic lead being formed.

W. A. D.

**Estimation of Potassium in Fertilisers.** By CARL G. EGGERTZ and LARS F. NILSON (*Zeit. anal. Chem.*, 1899, 38, 172—173; from *Kongl. Landtbruks-Akad. Hand. och Tidskrift*, 35, 326).—The authors have endeavoured to clear up the discrepancies which Atterberg and others (*Abstr.*, 1897, ii, 160) assert to exist between the results of the Stassfurth and the Swedish methods of estimating potassium, and find that both methods, when applied to kainite, give closely concordant results. In assaying calcined salts, the differences are slightly greater, but still quite unimportant. They attribute the lower results obtained in Sweden mainly to the fact that the Stassfurth salts, especially after calcination, are highly hygroscopic, and insist on the necessity of estimating moisture in all cases. A defect in both methods, however, is that the substance is dissolved by dilute hydrochloric acid, whereas it has been agreed, by the meeting of German chemists at Kiel in 1895, that only the potassium soluble in water should be estimated; the insoluble portion should therefore be removed before acidifying. The quantity of acid prescribed in the Swedish method (1 c.c. of dilute acid to 10 grams of substance) is insufficient, and permits a considerable

amount of potassium to adhere to the precipitate of barium sulphate obtained when freeing the solution from sulphates; the substitution of 1 c.c. of fuming acid for this quantity is recommended. To test the weighed platinochloride for impurities, they treat the weighed precipitate with 1 c.c. of water of atmospheric temperature, remove this instantly by suction, wash with 1 c.c. of absolute alcohol, and lastly with 1 c.c. of ether, evaporate the solution, and dry for 10 minutes at  $130^{\circ}$ . A larger residue than 7 milligrams indicates impurities. M. J. S.

**Estimation of Calcium Carbonate in Marl and Soil.** By ADOLF MAYER (*Landw. Versuchs-Stat.*, 1899, 51, 339—340).—The usual method, depending on the liberation of the carbonic anhydride which is then estimated from the loss in weight or else gravimetrically or gasometrically, generally gives satisfactory results. Varieties of marls exist, however, which contain more or less ferrous carbonate and some even effervesce, when treated with hydrochloric acid, although only traces of calcium carbonate are present.

Satisfactory results are obtained when acetic acid (diluted with two parts of water) is used instead of hydrochloric acid; with pure lime marls, results are obtained with Scheibler's apparatus agreeing with those obtained with hydrochloric acid, whilst ferrous carbonate is not appreciably attacked. The marl must be finely powdered.

The modification is of great practical importance, since by it the presence of impurities in marl is readily detected; marls containing ferrous carbonate are quite unsuited for applying to the land, as the ferrous salt would utilise the oxygen of the soil and thus diminish its neutralising power towards weak acids. N. H. J. M.

**Formaldoxime as an Agent for detecting Traces of Copper.** By A. BACH (*Compt. rend.*, 1899, 128, 363—365).—Formaldoxime hydrochloride,  $(\text{CH}_2\text{:NOH})_3\text{HCl}$ , obtained by the action of formaldehyde on hydroxylamine hydrochloride, or of trioxymethylene on hydroxylamine hydrochloride, and identical with that described by Dunstan and Bossi (*Trans.*, 1898, 353), gives a very intense violet coloration even with very dilute solutions of cupric salts, and can detect one part of cupric sulphate in 1,000,000 parts of water.

The reagent is prepared by adding a molecular proportion of hydroxylamine hydrochloride to formaldehyde in solution (1:5); after mixing it with the copper solution, a slight excess of potassium hydroxide should be added. The colour is somewhat similar to that produced by biuret, and it is noteworthy that the product of the action of concentrated formaldehyde solution on solid potassium cyanide gives the biuret reaction. C. H. B.

**Estimation of Mercury in Organic Liquids, and especially in Liquids fermented in presence of Mercuric Chloride.** By A. GAYON and L. LABORDE (*Ann. Agron.*, 1899, 25, 142—143; from *Rev. Viticult.*, 10, 177).—The wine (1 litre) is heated with pure nitric acid (150 c.c.) until the action becomes vigorous, when heating is discontinued. When cold, the clear yellow liquid is submitted to electrolysis, and in about 12—15 hours the whole of the mercury is

deposited. This is redissolved in a few c.c. of pure nitric acid, with the aid, if organic matter is present, of potassium chlorate (0.1—0.2 gram) and a few drops of hydrochloric acid; a little water is then added and the chlorine expelled by boiling. The cold solution is either neutralised with ammonia or is treated with ammonium acetate and acetic acid, and titrated with stannous chloride.

It was found in every case that, after fermentation, only minute traces of mercury remained in solution; the rest, having been rendered insoluble, was found in the deposit. It is concluded that newly made wines from the grapes of vines treated with salts of mercury contain only harmless traces of mercury (compare De Cazeau, *Ann. Agron.*, 1898, 24, 42).  
N. H. J. M.

**The Amount of Carbon in Electrolytically Deposited Iron.** By HANS VERWER and FRIEDRICH GROLL (*Ber.*, 1899, 32, 806—809).—The authors do not agree with the conclusions of Avery and Dales (this vol., ii, 251), that the use of ammonium oxalate in the electrolysis of iron salts causes the separation of carbon at the cathode and, further, leaves some of the iron unchanged in the solution. They have carried out a number of experiments, and find that in no case is the percentage of iron too high, and that the solution after the electrolysis does not contain unchanged iron salt. J. F. T.

**Electrolytic Estimation of Nickel in presence of Iron.** By B. NEUMANN (*Chem. Zeit.*, 1898, 22, 731).—In order to avoid the repeated dissolution and reprecipitation needful in separating iron and nickel by ammonia, it has been proposed to precipitate the nickel by electrolysis from the ammoniacal nickel sulphate solution containing suspended ferric hydroxide. The nickel thus obtained is shown to contain an amount of iron which varies with the quantity of iron suspended and with the duration of the electrolysis. If ferrous iron is present, the quantity in the nickel deposit is much increased. The following process is sufficiently accurate for technical purposes: 5 grams of nickel steel are dissolved in dilute sulphuric acid, the iron oxidised with hydrogen peroxide or bromine, and precipitated by ammonium sulphate and ammonia. After boiling, excess of ammonia is added and the solution diluted to 500 c.c.; 100 c.c. are filtered off, warmed to 50—60°, and electrolysed with a current density of 1 to 2 ampères per square decimetre and 3.4 to 3.8 volts. The electrolysis is complete in  $1\frac{1}{2}$  to 2 hours, and the results are satisfactory. Nickel mattes are dissolved in hydrochloric acid, nitric acid being subsequently added, and the solution evaporated with sulphuric acid until white fumes appear; after removal of copper, arsenic, and antimony in the usual way, the solution is treated as before. In this case, nickel and cobalt are deposited together. T. E.

**Volumetric Estimation of Bismuth by Alkaline Arsenite.** By C. REICHARD (*Zeit. anal. Chem.*, 1898, 38, 100—101).—The bismuth is converted into bismuthic acid, either by adding an excess of alkali to the solution of a bismuthous salt and passing a current of chlorine, or by adding the bismuthous salt directly to a hot mixture of sodium hypochlorite and hydroxide. After boiling until the precipitate has

acquired a deep red colour, it is thoroughly washed by decantation. A known excess of a solution of arsenious anhydride in sodium hydroxide is then added; the more concentrated this solution, the more rapid will be the reduction. The mixture is boiled until the red precipitate has been completely reduced to white bismuthous hydroxide; sulphuric acid is then added until the reaction is strongly acid, and the precipitate is removed by filtering hot. The residual arsenious acid in the filtrate is then titrated by permanganate. It is shown that the results obtained are concordant, but no proof of their correctness is given.

M. J. S.

**Detection of Iodoform in Aqueous Solution.** By LUDWIG VON STUBENRAUCH (*Chem. Centr.*, 1898, ii, 1285).—See this vol., i, 398.

**Action of Carbonic Anhydride on Potassium Ferrocyanide.** By GUIDO GIGLI (*Chem. Zeit.*, 1898, 22, 775—776).—When a cold solution of potassium ferrocyanide is saturated with carbonic anhydride, only a very slight turbidity is produced, but, on boiling, hydrocyanic acid is evolved, and a greenish precipitate, probably  $K_2Fe_2(CN)_6$ , is formed in small amount. If this is filtered off and the treatment renewed, fresh quantities of hydrocyanic acid and the greenish precipitate are formed. It seems probable that the carbonic anhydride in presence of water forms salts in which a portion of the potassium of the ferrocyanide is replaced by hydrogen, and that when the liquid is boiled these decompose, giving rise to hydrocyanic acid and the greenish-coloured potassium ferrous ferrocyanide. It follows, therefore, that the method proposed by Fresenius for detecting potassium cyanide in potassium ferrocyanide by the formation of hydrocyanic acid when the solution is treated with carbonic anhydride and distilled, is valueless. Sulphurous acid acts similarly to carbonic anhydride, but more energetically.

A. H.

**Action of Dilute Acids on Potassium Ferrocyanide.** By WILHELM AUTENRIETH (*Chem. Zeit.*, 1898, 22, 866—867).—The author points out that the decomposition of potassium ferrocyanide by carbonic and other weak acids described by Gigli (preceding abstract), has been fully studied by him (*Kurze Anleitung zur Auffindung der Gifte*, 1892, s. 8), and recognised by Fresenius (*Anleitung zur Qualitativen Analyse*, 1895, 306). The only process available for the detection of potassium cyanide in potassium ferrocyanide is that of Jacquemin, in which the sample is distilled with sodium hydrogen carbonate, which liberates hydrocyanic acid from cyanides, but not from ferrocyanides.

A. H.

**Detection of Methylic Alcohol in Spirits: Presence of this Alcohol in Brandy from Marc.** By AUGUSTE TRILLAT (*Compt. rend.*, 1899, 128, 438—440).—The author has applied his method for the detection of methylic alcohol (this vol., ii, 130) to various spirits. Fifty c.c. of the spirit was mixed with 50 c.c. of water and 8 grams of calcium oxide and fractionated; the first 15 c.c. was diluted to 150 c.c., oxidised by means of 15 grams of potassium dichromate and 70 c.c. of dilute sulphuric acid (1:5), and treated in the manner previously described (*loc. cit.*). In the case of liquids like absinthe, 50 c.c. was

mixed with 50 c.c. of water and 2 to 3 grams of calcium hydroxide, filtered through animal charcoal, and distilled as above.

Genuine rum, arrack, kirschwasser, absinthe, and cognac were found to be free from methylic alcohol, and this, in the case of rum, confirms the statements of Prinsen Geerligs; low priced samples of the same spirits, however, were found to contain proportions of methylic alcohol representing the addition of from 5 to 15 per cent. of methylated alcohol.

Some samples of brandy from marc were found to be free from methylic alcohol, whilst others contained it, probably as a result of defective distillation.

C. H. B.

**Colour Reaction for Methylic Alcohol.** By S. P. MULLIKEN and H. SCUDDER (*Amer. Chem. J.*, 1899, 21, 266—271).—A piece of light copper wire is wound into a close spiral about 2 cm. in length; it is superficially oxidised in the Bunsen flame and, whilst still red hot, is plunged into 3 c.c. of the liquid placed in a test-tube; a second dip is advisable, and with solutions containing less than 0.1 per cent. of methylic alcohol three or four additional dips are necessary, the tube being cooled after each. A concentrated spirit should always be diluted with at least 3—4 volumes of water before oxidation. The formic aldehyde produced is detected by the aid of a 0.5 per cent. aqueous solution of resorcinol. One drop of the solution is added to the oxidised methylic alcohol and the mixture very cautiously poured down the side of a test-tube containing a few c.c. of concentrated sulphuric acid, the presence of methylic alcohol in the suspected liquid being indicated by the appearance of a pure rose-red zone at the junction of the two liquids. Too large a quantity of resorcinol is to be avoided, as it tends to destroy the purity of the rose colour. Other substances which give similar colorations are secondary and tertiary butylic alcohols, dimethylethylcarbinol, formic acid, and most methylic salts and ethers. The colour with formic acid is extremely feeble. Other monohydric alcohols give ochreous yellow, and polyhydric alcohols give brownish-purple colorations.

J. J. S.

**Distinctive Reactions for Creosote and Guaiacol.** By H. FONZES-DIACON (*Bull. Soc. Chim.*, 1898, 19, [iii], 191—192).—The guaiacol present in commercial creosote may be estimated colorimetrically by treating a dilute solution of the specimen under examination with either sodium nitrite and nitric acid or with copper sulphate and potassium cyanide, and matching the coloration produced with that developed by these reagents in guaiacol solutions of known strength. In the absence of the standard solutions, a small quantity of the specimen is treated with 2—3 c.c. of 4 per cent. copper sulphate solution and 1—2 c.c. of potassium cyanide solution of the same strength; coloured striæ at once appear in the solution; these, when viewed by transmitted light, are green when guaiacol is absent; traces of this substance give rise to reddish-grey streaks, whilst larger quantities produce a brownish-purple coloration.

G. T. M.

**Estimation of the Quality of Sugar Beet.** By L. SEMPOLOWSKI (*Landw. Versuchs-Stat.*, 1899, 51, 341—349).—Roots from the

same seed, and growing on the same land, vary more or less in the amount of sugar they contain (even as much as 6 per cent.), and it is necessary in sampling to obtain at least 50 or 60 roots from a field. The most exact method is to take every 50th or 100th root, or if the number of roots is immaterial, a whole row of roots may be taken from a field, or even two rows at right angles to each other. After cutting off the heads, which must include the whole of the cells containing chlorophyll, small sections are rasped from the whole length of each root (Keil's segment rasper takes out about 9 per cent. of the weight of a root). A normal pulp, which should be very fine, remains unchanged for 12—24 hours.

As regards the employment of lead acetate solution, the ordinary amount is 2 c.c. to the normal weight of pulp; it should be added to the flask with the pulp, which is thus rendered more porous. As much as 4 c.c. of lead acetate may be added without loss of sugar. Water extracts require plenty (5—6 c.c.) of lead acetate solution.

Instead of employing dishes, the recommendation is made that the pulp should be weighed directly in flasks with wide necks.

It has recently been stated that, in the selection of seed by the usual method, sugar beet is obtained which contains a high percentage of raffinose. The amount of raffinose is, however, only slight (at most 0.02 per cent.), and the examination of five samples of roots of high percentage showed no considerable difference between the direct and the inversion method.

As the chemical methods present no difficulties, special attention must be given to obtaining large samples of roots from which thin, representative sections must be properly rasped so as to obtain a fine pulp.

N. H. J. M.

**Detection of Aloes.** By ALOIS KREMEL (*Zeit. anal. Chem.*, 1899, 38, 193—195; from *Erstes Decennium der Helfenberg. Annalen*, 6).—Solid substances are exhausted with alcohol, alcoholic or aqueous solutions are evaporated on the water-bath, and the residues dissolved in water or alcohol respectively. The latter solution is again evaporated and the residue taken up with water; the aqueous solution being then precipitated with excess of basic lead acetate and the excess of lead removed from the filtrate by sodium sulphate. By these operations, all substances which interfere with the reactions are removed. The special reactions for aloin may then be applied. One of the most characteristic is the conversion into chrysammic and picric acids; the solution is evaporated to dryness and the residue digested for some hours with 6 parts of concentrated nitric acid of sp. gr. 1.45, 3 parts of water are added, and the solution heated on the water-bath. On the further addition of water and cooling, the chrysammic acid separates in deep yellow to orange crystals. Chrysammic acid may be identified by the carmine-red colour of its alkali salts, the violet colour of its ammonium salt, and the insolubility of its barium salt. The picric acid is recognised by dyeing wool yellow.

M. J. S.

**Evaluation of Secale Cornutum (Ergot of Rye).** By HEINRICH BECKURTS and W. GROTHE (*Zeit. anal. Chem.*, 1899, 125—126; from *Zeit. allgem. oesterr., Apoth.-Vereins*, 50, 31), and by C. C. KELLER (*Schweizer Wochenschr. Pharm.*, 894, 121).—In estimating the cornutine

present, the fatty oil must first be removed; the drug is, therefore, reduced to coarse powder and thoroughly exhausted with light petroleum. After drying, the substance is shaken with 100 grams of ether and 1 gram of magnesia, previously mixed with 20 c.c. of water, and left for three or four hours; 60 grams of the clear, ethereal solution are then removed, and shaken in a separating funnel successively with 25, 15, 10 and 10 c.c. of 0.5 per cent. hydrochloric acid. The acid solution is then supersaturated with ammonia and again shaken with ether; when evaporated, this ethereal solution leaves the cornutine. Various specimens yielded from 0.1 to 0.2 per cent., and as a rule those dried over quicklime gave a larger yield than those kiln-dried at 50°.

M. J. S.

**Precipitation of Urea by Phosphotungstic Acid.** By ALLYRE CHASSEVANT (*Bull. Soc. Chim.*, 1898, 19, 255—256).—With solutions containing more than 2 per cent. of urea, phosphotungstic acid produces a precipitate, which, however, dissolves on diluting with water; in using Pflüger's method for precipitating substances other than urea from urine, care must, therefore, be taken that the solutions are sufficiently dilute to prevent any of the latter being thrown down. W. A. D.

**Estimation of Alkaloids by means of Standard Iodine Solution.** By MAX SCHOLTZ (*Arch. Pharm.*, 1899, 237, 71—80).—This paper describes an experimental examination of Kippenberger's methods (Abstr., 1895, ii, 467; 1896, ii, 282, 682), and concludes with the words: (1) The theoretical considerations upon which Kippenberger's methods are based are in contradiction with elementary chemical laws. (2) Kippenberger's analytical results cannot for the most part be obtained under the conditions employed by him. (3) The methods recommended by Kippenberger for the quantitative estimation of alkaloids by means of standard iodine solution are worthless.

C. F. B.

**Estimation of Caffeine in Tea, Coffee, and Kola.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 58—68).—The method of Hilger-Juckenack (*Forschungsber. ii. Lebensmittel, &c.*, iv., 49, 145) gives a lower percentage of caffeine in all cases than that of Keller (Abstr., 1898, ii, 269). This is because the caffeine is not entirely extracted by the boiling water; the author finds that 3 hours boiling does not effect complete extraction. Keller's method is simple, rapid, and gives very good results.

As regards coffee, it has already been shown that Keller's methods, slightly modified, may be used with the raw material (Siedler, *Ber. deut. pharm. Ges.*, 1898, 8, 19). The author now shows that it may be used with the roasted berries; here again the Hilger-Juckenack method gives lower results.

As regards kola, Keller's method gives (as in the case of tea) the same result whether ammonia be used, or water in its stead. Hence, if the dry material does contain "combined" caffeine, probably in the form of a tannate, the compound is at once decomposed by water. For all practical purposes, then, it is useless to insist on the distinction between "free" and "combined" caffeine; the distinctive effect of kola-nut preparations must be due to the presence of yet other substances.

C. F. B.



**Modification of the Thalleioquinine Test.** By EGIDIO POLACCI (*Chem. Centr.*, 1898, ii, 1221; from *Pharm. Post.*, 31, 509).—Lead dioxide may be used instead of chlorine water when testing for quinine. One gram (1.001 gram) of the substance is put into a test-tube and dissolved in 1 c.c. of water and two drops of dilute sulphuric acid; the blue fluorescence is in itself a proof of the presence of quinine. A small quantity of lead dioxide is added, the mixture well shaken, and after heating thrice to boiling, 4 c.c. of water is added; when the liquid has become clear, a few drops of ammonia are carefully run in when a splendid emerald-green ring is formed if quinine is present.

L. DE K.

**Estimation of Alkaloids in Cinchona Bark.** By WILHELM LENZ (*Zeit. anal. Chem.*, 1899, 38, 141—154).—The methods hitherto published are all more or less open to objection. That prescribed by the German Pharmacopœia, and that of Haubensack (*Abstr.*, 1891, 1402), as modified by Keller, both give results varying with the degree of fineness to which the bark is pulverised, in consequence, apparently, of the feeble penetration of the cells by the solvent employed; with the former the results are in all cases too low, whilst with the latter, they are impaired by the impurity of the product. In the methods of Meyer (*Abstr.*, 1883, 388) and Hielbig (*Zeit. anal. Chem.*, 1881, 20), the products are very impure, and there is a risk of the destruction of some of the alkaloids by the very powerful agents (lime and sulphuric acid) employed. With the object of breaking down the cell-walls by a reagent which does not decompose quinine, the author advocates the use of an aqueous solution of chloral hydrate. Ten grams of the powdered bark are macerated for 12 hours with a solution of 20 grams of chloral hydrate in 12.5 grams of water, and are then cohobated for half an hour with 150 c.c. of 61 per cent. alcohol, and 2 grams of 25 per cent. hydrochloric acid. The solution is filtered through glass wool, and the residue well washed with the same acidified alcohol; the filtrate and washings are evaporated to a syrup, which is then triturated with a little water and hydrochloric acid, so as to precipitate the resin in the form of fine flocks. By filtering a known portion of this mixture, the washing of the resin may be dispensed with. The acid filtrate is made alkaline with sodium hydroxide, and immediately shaken with chloroform, of which 100, 50, and 50 c.c. suffice to remove all the alkaloids. The chloroform solution is shaken thrice with 2 per cent. hydrochloric acid (100, 50, and 50 c.c.) and once with 50 c.c. of water, and this acid solution is made alkaline and shaken with ether so long as anything is removed thereby. The treatment with ether, and especially the withdrawal of the ethereal layers, must be done rapidly, lest sparingly soluble alkaloids should be precipitated. The ether is distilled off, and the residue dried at 100°. The estimation of the quinine in the products of the above five processes by conversion into iodo-sulphate according to De Vrij (*Abstr.*, 1876, i, 964) showed that the chloral process gave a result agreeing closely with that of Haubensack-Keller, and higher than any of the others, and the method is independent of the extent to which the bark is pulverised.

M. J. S.

**Discrimination of Eucaïne and Cocaine.** By GUSTAVE VULPIUS (*Zeit. anal. Chem.*, 1899, **38**, 197; from *Pharm. Centralhalle*, **37**, 295).—A decigram of the substance is dissolved in 50 c.c. of water of 18—20° in a graduated cylinder and gently mixed with two drops of aqueous ammonia. A pure cocaine salt will remain clear for at least a minute, and even if on vigorous shaking crystals of cocaine separate, the liquid does not lose its transparency. In presence of 2 per cent. of eucaïne, a strong, milky turbidity is immediately produced by the ammonia, and only disappears on adding 10 c.c. more water; with 5 per cent. of eucaïne, 20 c.c. of water must be added.

M. J. S.

**A Delicate Test for Solanine, and the amount Yielded by Potatoes.** By BAUER (*Zeit. angew. Chem.*, 1899, 99—100).—The quantity of solanine was estimated by the process devised by Meyer, the potatoes being first boiled in their skins. The crop from 1897 yielded 0.002, and that from 1898, 0.0026 per cent. of the alkaloid.

The following test for the alkaloid exceeds in delicacy the usual test with selenic sulphuric acid. If solanine is heated on the water-bath with a solution of telluric acid in moderately concentrated sulphuric acid, a fine raspberry-red colour is developed, which lasts for two or three hours. Other alkaloids, such as atropine, morphine, and quinine, are not affected.

L. DE K.

**Egg-albumin and Yolk of Egg.** By KARL DIETERICH (*Chem. Centr.*, 1898, ii, 1283—1284; from *Pharm. Centr.-H.*, **39**, 789—794. Compare *Abstr.*, 1898, i, 390).—White of egg contains 7—17.5 per cent. of water, and has an iodine absorption number = 110—170, that of the anhydrous albumin being 150—170. In determining the iodine number, the albumin should be completely dissolved by allowing it to remain with water overnight. Ordinary egg-albumin contains less than 1 per cent. of fat, but albumin from which the yolk has been incompletely separated has a higher content. To test for gum, dextrin, gelatin, abnormal treatment, &c., 1 gram of the air-dried substance is dissolved in 50 c.c. of water, and the solution allowed to remain 3 days in a closed vessel with a volume of a standard solution of iodine equal to 20 c.c. of a decinormal solution of sodium thiosulphate. It should then not require more than 11 c.c. or less than 6.5 c.c. of the sodium thiosulphate solution. The amount of water in white of egg is determined by drying at 100°, and the ash should not be more than 6 per cent. Insoluble substances such as fibrin are weighed on tared papers.

To test yolk of egg, the fibrin, albumin, yolk, and egg-oil are each isolated, and the iodine absorption number of each determined. The fibrin, which amounts to about 1 per cent., is separated from the yolk by beating, filtering through cloth, and drying. The soluble albumin is carefully evaporated and dried at 30°. The yolk, freed from fat and separated from the egg-oil by ether, has a very pale colour.

E. W. W.

## General and Physical Chemistry.

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**Atomic Refraction of Metals in Carbonyl Compounds, and the Constitutional Formulæ of these Derivatives.** By ANTONIO J. FERREIRA DA SILVA (*Bull. Soc. Chim.*, 1898, 19, [iii], 441—445. Compare Abstr., 1891, 1322).—In reply to Nasini (Abstr., 1898, ii, 274), the author objects to the interpretation put on his former statements (Abstr., 1897, ii, 406), and shows by reference to this investigator's data that the molecular refraction of organic and metallic carbonyl compounds cannot be an additive property. Assuming that the atomic refraction of the elements combined with carbonyl is normal, the molecular refraction of this radicle varies from 9.13 to 18.39.

G. T. M.

**Optical Isomerism.** By PAUL WALDEN (*Chem. Centr.*, 1898, ii, 917—918; from *J. Russ. Chem. Soc.*, 30, 483—545).—A summary of the papers bearing on the subject of optical isomerism, published in the *Berichte* and *Zeit. physikal. Chem.* since 1893, with special reference to methods of preparation and theoretical inferences (compare Abstr., 1893, i, 250; 1895, ii, 65, 149; 1896, i, 205; ii, 553, 633; 1898, i, 176, 178; ii, 149). The new matter here collected is concerned mainly with chlorosuccinic, bromosuccinic, chloromalic, phenylchloracetic, and chloropropionic acids and their derivatives.

E. W. W.

**Radiations from Uranium and other Substances.** By HENRI BECQUEREL (*Compt. rend.*, 1899, 128, 771—777).—The intensity of the radiations from uranium and its compounds shows no appreciable variation after three years, although during the whole of this time they have been enclosed in a wooden box encased with lead. There was some indication of a slight diminution in the intensity of the radiation during the first two or three months under these conditions, but the evidence was not conclusive, and the intensity remained constant subsequently. Two of the earlier observations with uranium indicated that the rays can be polarised by tourmaline, but subsequent observations with uranium, and also with radium and polonium, have failed to confirm this result. Many experiments showed apparent reflection of the radiations from uranium, radium, and polonium from the surface of many metals, wood, glass, paper, paraffin, and other substances. No appreciable differences were observed between rough and polished surfaces, and no reflection of definite images could be obtained, and the experiments do not distinguish decisively between diffuse reflection and secondary radiation. Possibly both causes operate simultaneously, but whichever it may be, the intensity of the effects observed is not affected by reducing the pressure of the surrounding atmosphere to 20 mm. In some conditions, the photographic effect of the apparently reflected rays is greater than that of the direct radiation, and this result seems to indicate the occurrence of secondary radiation.

Some evidence was obtained of refraction of the rays at vertical edges of sheets of glass, mica, paper, and other substances, but, on the

other hand, the radiations were found to pass without deviation through prisms of glass and metals, absorption taking place in proportion to the thickness of the material.

The radiations from various substances are not only unequal in intensity, but are absorbed by different substances in different degrees. The radiations from uranium and radium show practically the same absorption phenomena, although those from radium are the more intense. The rays from polonium pass much less rapidly through paper, mica, calcite, or quartz than the rays from radium. Thin sheets of aluminium are more transparent to rays from polonium than to those from uranium, but with thick sheets (2 mm.) the converse is the case.

The radiations from uranium, radium, polonium, and thorium resemble Röntgen rays much more than ordinary light. Hitherto, however, it has not been found possible to change the intensities of the radiations by physical influences. The radiating substances seem to be analogous to ordinary phosphorescent materials, but to retain relatively a very much greater reserve of energy.

C. H. B.

[Zinc Sulphide Actinophotometer.] By CHARLES HENRY (*Compt. rend.*, 1899, 128, 941—944).—A photochemical paper discussing the advantages of the author's zinc sulphide actinometer for photographic purposes.

G. T. M.

Variance of the Voltaic Cell. By WILDER D. BANCROFT (*J. Physical Chem.*, 1898, 2, 427—440).—In applying the phase rule to voltaic cells, the E.M.F. appears as a variable in addition to the temperature, the pressure, and the concentration of the solutions. The variance of the whole cell  $V = \Sigma v$ , where  $\Sigma v$  is the sum of the variances of the separate elements of the cell. If the temperature and pressure of the cell are uniform for all the elements, then  $V = \Sigma(v - 2) + 2$ . Thus, for the Clark cell,  $\text{Zn} \mid \text{ZnSO}_4\text{aq.}, \text{Hg}_2\text{SO}_4 \text{ (solid)} \mid \text{Hg}$ ,  $V = (0 + 1 + 0) + 2 = 3$ , the E.M.F. varying with the temperature, the pressure, and the concentration of the zinc sulphate solution; for the Daniell cell,  $\text{Zn} \mid \text{ZnSO}_4\text{aq.} \mid \text{CuSO}_4\text{aq.} \mid \text{Zn}$ ,  $V = (0 + 1 + 1 + 0) + 2 = 4$ . The effect of concentration on the E.M.F. can be determined from the theorem of Le Chatelier, that on passing a current the concentration will change in such a manner as to oppose a maximum counter E.M.F.; thus when the current flows through a cell in such a direction that zinc passes into a zinc sulphate solution, the E.M.F. will be increased by diluting the zinc sulphate, and *vice versa*. The E.M.F. will increase with the pressure if the volume of the cell decreases with the passage of the current, as was predicted by Gibbs and verified by Gilbault (*Compt. rend.*, 1891, 113, 465). The effect of temperature can be deduced in a similar way.

T. M. L.

Electromotive Force between Amalgams. By HAMILTON P. CADY (*J. Physical Chem.*, 1898, 2, 551—564).—The electromotive force between two amalgams of different concentrations is independent of the concentration of the electrolyte and of the solvent used in preparing it; this has been verified with zinc and calcium amalgams, using as the electrolyte solutions of zinc chloride, calcium chloride, or

calcium iodide in water, alcohol, or pyridine. The electromotive force is calculated from the formula  $E = 0.0002 \cdot (T/\nu) \log_{10}(c_1/c_2)$ , where  $T$  is the absolute temperature,  $\nu$  is the valency of the metal in the electrolyte, and  $c_1$  and  $c_2$  are the concentrations of the two amalgams. Using this formula, normal results are obtained with zinc, lead, tin, copper, and cadmium amalgams (Meyer, *Abstr.*, 1891, 984), but the alkalis and alkaline earths are found to give much greater values for the E.M.F. than those calculated from the formula. It is shown that the heat of dilution of the amalgam, which is usually assumed to be zero, must be introduced into the formula, which then becomes  $E = q + 0.0002 \cdot (T/\nu) \log_{10}(c_1/c_2)$ , where  $q$  is the electrical equivalent of the heat of dilution. The value of  $q$  has been determined for a sodium amalgam, and the corrected formula is found to give results which agree closely with the observed values of the electromotive force.

Similar abnormal results have been obtained by Ramsay (*Trans.*, 1889, 56, 521) in determining the vapour pressures of mercurial solutions, and these can be explained in the same way as due to the presence of a large heat of dilution.

T. M. L.

**Electromotive Force between Amalgams. A Correction.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 107. Compare Cady, preceding abstract).—The work done in carrying a molecular weight of zinc from one amalgam to another is independent of the size of the molecule; the quantity of electricity required is, however, proportional to the number of atoms in the molecule. The E.M.F. of a concentration battery is therefore inversely proportional to the number of atoms in the molecule and not independent of it, as was stated in the paper referred to; the E.M.F. gives a measure of the complexity of the molecule, provided always that the heat of dilution of the amalgam is zero.

T. M. L.

**Electromotive Force of Concentration Cells.** By JOSEPH E. TREVOR (*J. Physical Chem.*, 1899, 3, 95—106. Compare preceding abstracts).—A mathematical investigation of the influence of the heat of dilution on the E.M.F. of concentration cells.

T. M. L.

**Electrometric Determinations of Constitution.** By RICHARD KIESERITZKY (*Zeit. physikal. Chem.*, 1899, 28, 385—423).—The dissociation of a number of compounds of mercury with various nitrogenous organic substances was determined by the measurement of the difference of potential between a mercury electrode and a solution of the compound in a suitable solvent, usually N/10 potassium sulphate; Poggendorff's method with a Lippmann electrometer was used, the current being obtained from an accumulator, the E.M.F. of which was from time to time determined by comparison with that of a Weston cell. The mercury derivatives of the following compounds were investigated: triglycolamic acid, diglycolamic acid, hippuric acid, glycocine, acetamide, propionamide, benzamide, carbamide, salicylamide, oxamide, malonamide, succinamide, succinimide, hydrogen cyanide, alloxan, alloxantin, parabanic acid, uric acid, dibenzamide, phthalimide, cyanuric acid, and nitrous acid. As a general rule, the concentration of the mercury ions is greatest in the carboxy-

compounds and is greater for the amido- than for the imido-compounds. This generalisation may be of value in determining the constitution in doubtful cases. The E.M.F. of mercury glycocine agrees with that of mercury acetamide and mercury propionamide, and hence the metal is most probably united to the nitrogen in this compound. In mercury cyanide also, the mercury is combined with nitrogen, so that hydrogen cyanide is an imido-compound and the direct derivatives are the isonitriles. Mercury succinimide is also a true imido-compound, and hence the silver compound, which behaves similarly, has most probably an imido-compound, although by the action of alkyl iodides the unsymmetrical alkyl derivatives of succinimide are obtained; the correctness of the usually accepted constitutional formula of these compounds is therefore doubtful. Nitrous acid also appears to be an imido-compound, so that the nitroparaffins are its direct derivatives and the nitrites the iso-compounds. These views of the constitution of hydrogen cyanide and nitrous acid are not in accord with those of Brühl, based on the refraction and dispersion of the compounds (*Abstr.*, 1895, ii, 250; 1898, ii, 362). Incidentally, the formation of a thick jelly by the addition of various salts to mercury acetamide was noticed, but not investigated.

L. M. J.

**Law of the Dilution of Electrolytes.** By PAUL TH. MULLER (*Compt. rend.*, 1899, 128, 505—507).—Ostwald's law concerning the influence,  $\delta$ , of the concentration on the difference between the molecular conductivity of a solution of given strength and that of an infinitely dilute solution, and Kohlrausch's law of the decrease in the mobility of the ions with an increase in concentration (this vol., ii, 201) become identical if it is assumed that the anions and kations exert the same influence on the value of  $\delta$ . In Kohlrausch's numbers, the quotients  $\delta_\nu/\delta_{2\nu}$  have practically the same value, 1.333, and if  $\nu$  is taken as  $2^n$ , the value of  $\delta$  (after eliminating  $n$ ) is  $\delta = A\nu^{-(0.41504)}$ , where  $A$  is a constant. Assuming 52.72 as the value of this constant, the equation reproduces Kohlrausch's results with considerable accuracy. The molecular conductivities  $\mu$  at 18° of normal salts formed by univalent ions are given by the formula  $\mu = \mu_\infty - 52.72\nu^{-(0.41504)}$ . In the case of Bredig's results (*Abstr.*, 1894, ii, 226), the value of  $A$ , at 25°, is 62.152, and hence it is possible to calculate the conductivity  $\mu_\infty$  if some values of  $\mu$  are known for any dilution (higher than 30 litres per gram-molecule) at 18° and 25°.

C. H. B.

**Conductivity of Mixtures of Electrolytes.** By F. BARMWATER (*Zeit. physikal. Chem.*, 1899, 28, 424—430).—Expressions are deduced for the conductivity of solutions of two or more electrolytes, and the applicability of these expressions is proved by determination of the conductivity in the case of mixtures at various concentrations of sodium and potassium chlorides; sodium chloride and potassium iodide; sodium chloride and potassium nitrate; potassium chloride and nitrate; sodium and potassium chlorides and potassium nitrate; and sodium and potassium chlorides, potassium nitrate and potassium iodide. The expressions are based on the previous deductions of the

author (this vol., ii, 274), are simple, and in all cases yield values in good accord with the observations. L. M. J.

**Dissociative Power of Solvents.** By LOUIS KAHLENBERG and AZARIAH T. LINCOLN (*J. Physical Chem.*, 1899, 3, 12—35).—In order to ascertain the conditions which are necessary for the production of an electrolyte, the authors have determined to what extent ferric chloride, antimonious chloride, bismuth chloride, and mercuric chloride are capable of yielding conducting solutions when dissolved in various organic and inorganic solvents. The hydrocarbons and their halogen substitution products do not give conducting solutions. Alcoholic solutions conduct well comparatively, but less so in the higher members of the series; phenols give solutions which conduct less than the alcohols. Ethers and acid anhydrides yield solutions of very low conductivity, whilst carbon bisulphide does not give conducting solutions. Aldehydes and ketones give conducting solutions, but chloral forms an exception, and gives non-electrolytic solutions. Ethereal salts, and especially the higher homologues, give solutions of very low conductivity; substitution of Cl, CN, or  $\text{CH}_3\cdot\text{CO}$ , tends to increase rather than decrease the conductivity. Oxidised nitrogen compounds, nitriles and cyclic compounds containing nitrogen give conducting solutions, but phenylhydrazine and aromatic amines give non-conducting solutions. Arsenic trichloride gives conducting solutions, but not phosphorus trichloride. A table is given in the paper showing in detail the results obtained with 72 different solvents, and measurements are given of the conductivity of a number of solutions in methylic and ethylic alcohols, acetone, ethylic acetate and acetoacetate, benzaldehyde, and nitrobenzene.

By far the larger number of solvents which give electrolytic solutions have a high dielectric constant, whilst solvents of low dielectric power do not give conducting solutions; Nernst's hypothesis that there is an intimate connection between these two properties is therefore entirely confirmed. Many of the solvents, however, which give conducting solutions have a very low coefficient of association, and are not polymerised to any appreciable extent; Dutoit and Aston's hypothesis (*Abstr.*, 1897, ii, 546) cannot therefore be maintained. Brühl's hypothesis (*Abstr.*, 1895, ii, 163), that conductivity depends on the residual affinity of tetrad oxygen, pentad nitrogen, &c., is contradicted by the want of conductivity of solutions in ether, ethylic carbonate, chloral, the aromatic amines, phenylhydrazine, and phosphorus trichloride; moreover, the substitution of the unsaturated cyanogen group for hydrogen in ethylic acetate does not produce any marked increase in the conducting power of its solutions.

Molecular weight determinations by the cyroscopic method in nitrobenzene solution gave values which decreased with increasing concentration in the case of ferric chloride, antimony chloride, and stannic chloride, whilst increasing values were obtained in the case of arsenic, bismuth, and phosphorus trichlorides; in the former case, the molecular weight in dilute solution is considerably greater than the calculated value, and in the latter case considerably less. T. M. L.

**A Remarkable Class of Inorganic Acids and their Electrolytic Behaviour.** By WILHELM HITTORF and HEINRICH SALKOWSKI (*Zeit. physikal. Chem.*, 1899, 28, 546—555).—In the electrolysis of solutions of gold and platinum chlorides in those of other chlorides, the separation of the heavy metal at the cathode is considered to be due to secondary reactions. By the electrolysis of the compounds  $\text{PtCl}_4 \cdot \text{H}_2\text{O}$  and  $\text{AuCl}_3 \cdot \text{H}_2\text{O}$ , the authors show that the metal is contained in the complex acid ion and the transference ratios for the two compounds are determined; hence the chlorides of gold and platinum are intermediate between the ordinary metallic chlorides and those chlorides which are decomposed by the addition of water. L. M. J.

**Some Iodine Compounds.** By EUGENE C. SULLIVAN (*Zeit. physikal. Chem.*, 1899, 28, 523—545).—Diphenyliodonium hydroxide (Hartmann and Meyer, *Abstr.*, 1894, i, 242) is an alkaline compound, and has been stated to be a somewhat weaker base than ammonia; conductivity determinations, however, prove it to be comparable with sodium and potassium hydroxides, as it is very highly dissociated. This is also seen by the determination of its hydrolysing power, the velocity coefficient of the hydrolysis of methylic acetate induced by it being approximately equal to that induced by sodium hydroxide of equal concentration. The atomic refraction of iodine in these bases was determined and found to be somewhat higher than that of univalent iodine in organic compounds, and to be approximately equal to that of iodine ions, whilst in benzene iododichloride a still higher value obtains. This chloride also readily loses chlorine and is a powerful oxidising agent; by the comparison of the E.M.F. of a platinum electrode in a solution of the compound in  $\text{N}/2$  hydrogen chloride with that of a similar electrode in a solution of chlorine in the same solvent, its electrical potential was found to be somewhat less than that of the free gas. Similar determinations were made with rubidium iodochloride (*Abstr.*, 1893, ii, 67), and with iodine chloride, both compounds being found to have equal electrical potentials. Cryoscopic and conductivity determinations indicate that the last two compounds in hydrochloric acid solution do not completely decompose, but form complex ions. L. M. J.

**Transference Number of Hydrogen.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1898, 2, 496—497).—The determinations of the migration velocity of hydrogen in hydrochloric acid by Bein (*Abstr.*, 1898, ii, 533), Hopfgartner (*Abstr.*, 1898, ii, 151), and McIntosh (this vol., ii, 137), give the values 314, 324, and 333 respectively, taking the migration velocity of chlorine as 63. If, however, the value for hydrogen is calculated from the conductivity at infinite dilution, independently of the migration-velocity of chlorine, the values obtained are 294, 295, and 297, and agree fairly with the value, 290, given by Kohlrausch; the values for chlorine then become 59, 58, and 56, instead of 63. T. M. L.

**Dependence of the Transference Ratios of Salts on the Nature of the Dividing Membrane.** By WILLY BEIN (*Zeit. physikal. Chem.*, 1899, 28, 439—452).—A review of the various values



for transference ratios of salts obtained by different methods leads to the general conclusion that the relative velocity of the kation is in all cases less when a dividing membrane is used than when no such division is employed. This difference is most marked for animal membranes, and is small or negligible for porous clay divisions or for parchment paper. In order to test the correctness of this conclusion, the transference ratios of hydrogen, sodium, lithium, calcium, and cadmium chlorides were determined with various septa of (1) clay, (2) parchment paper, (3) fish bladder, or (4) gold beaters' skin, and in all cases the velocity of the kation is diminished by use of the two latter membranes. The values obtained by Hittorf and others with membranous septa are collected and compared with those obtained by the author (*Abstr.*, 1898, ii, 553). This influence of the membrane does not appear to depend on its general permeability, and the probable cause is briefly discussed; it may be due to a chemical activity of the membrane, which would hence possess the character of an acid, or to polarisation induced by the current in the membrane. In either case, the result is that membranes actually behave as partial semipermeable divisions.

L. M. J.

**Thermal Conductivity of Various Kinds of Glass.** By ADOLF WINKELMANN (*Ann. Phys. Chem.*, 1899, [ii], 67, 794—802).—The absolute values of the thermal conductivity of a number of different glasses obtained by Focke (*ibid.*, 132), do not agree with those previously obtained for the same materials by Paalhorn. After reviewing the results, the conclusion is drawn that it is impossible to decide which set is the more correct. The relative values agree fairly, and the differences are probably chiefly due to the different temperatures at which the observers worked, the dependence of the conductivity on temperature being very imperfectly known. The observations also show that two glasses nominally identical may differ considerably in respect of this and other physical constants, and hence, if identical glasses are required, they must be obtained from one melting.

L. M. J.

**Pressure Variation of the Latent Heat of Fusion.** By GUSTAV TAMMANN (*Ann. Phys. Chem.*, 1899, [ii], 67, 871—878).—The variations of the latent heat of fusion with temperature at constant pressure, and with pressure at constant temperature, are first deduced, and hence the alteration of the latent heat along the melting point curve. The most important factor is  $(c_l - c_p)$ , that is the difference between the specific heats in the liquid and solid states at the melting point. This expression is probably always positive, and the accuracy of those experiments of Brunner (*Abstr.*, 1894, ii, 439), for which the converse was found to obtain, is held to be doubtful.

L. M. J.

**Thermal Properties of Quicklime prepared at Different Temperatures.** By HENRI GAUTIER (*Compt. rend.*, 1899, 128, 939—941).—Four specimens of calcium oxide were prepared from pure calcite by heating the carbonate at 1000°, and at 1200°, in the oxyhydrogen flame, and in the electric furnace. The specimens prepared at the lower temperatures were more readily hydrated than those heated to

higher temperatures; the specimen which had been fused in the electric furnace was hydrated with extreme slowness. The heat of dissolution of the four preparations in 5 per cent. hydrochloric acid was determined by Berthelot's calorimetric method, and the purity of the specimen under investigation was gauged by acidimetric estimations of the excess of acid remaining in the calorimeter. These experiments indicate that, whatever be the temperature at which it is produced, the heat of dissolution of calcium oxide in hydrochloric acid is the same, the mean value for 5 per cent. acid being 46.48 Cal. This result accords with the observation made by Berthelot, that the heat of formation of magnesia is the same whether this oxide be prepared at 440° or at a bright red heat. G. T. M.

**Heats of Combustion and Formation of Organic Compounds.**  
By MARCELLIN P. E. BERTHELOT and GUSTAVE ANDRÉ (*Compt. rend.*, 1899, 128, 959—971).

Substance.	Heat of combustion.		Heat of formation.	Heat of solution.
	At constant volume.	At constant pressure.		
Cholesterol.....	3836.4 Cal.	3843.0 Cal.	127.9 Cal.	
Glycollonitrile.. ..	257.1	257.0	36.0	- 0.11 Cal.
Lactonitrile .....	421.15	421.3	36.0	0.36
Xanthine.....	516.0	512.8	96.7	
Paraphenylenedi- amine.....	843.3	843.9	- 2.1	
Nicotine .....	1426.5	1428.0	{ liq. - 1.9 diss. + 5.15 }	7.05
Pyrroline .....	567.6	568.1	- 13.1	
Carbazole .....	1474.8	1477.0	- 34.9	
Indole .....	1021.8	1022.5	- 26.5	
Scatole .....	1169.7	1170.7	11.5	
α-Methylindole....	1167.9	1168.9	- 9.7	
Oxindole.....	950.45	950.8	45.1	

$C_2H_5NO$  liq. (glycollonitrile) +  $H_2O$  liq. =  $C_2H_5NO_2$  cryst. (glycollamine) + 19.1 Cals.

$C_2H_5NO$  liq. +  $2H_2O$  liq. =  $C_2H_4O_3 \cdot NH_3$  diss. + 16.8 Cal.

$C_3H_5NO$  liq. (lactonitrile) +  $H_2O$  liq. =  $C_3H_7NO_2$  cryst. (alanine) + 32 Cal.

$C_3H_5NO$  liq. „ +  $2H_2O$  liq. =  $C_3H_6O_3 \cdot NH_3$  diss. + 19.1 Cal.

A comparison of the heats of formation of indole, oxindole, and dioxindole indicates that the addition of the first oxygen atom is accompanied by development of heat, which is double that produced by the introduction of the second. The addition of another oxygen atom gives rise to isatic acid; the heat effect has not, however, been directly estimated, owing to the instability of the acid, but when calculated from the equation for isatin, the corresponding lactone, it is found to be 48.6 Cal.; it is therefore greater than that produced by the addition of the second atom. The reaction is, however, more complex, and isatin may really be a polymeride of the substance represented by the formula  $C_8H_5NO_2$ . G. T. M.

**Thermodynamical Expressions for the Heat of Dissolution and of Dissociation of Electrolytes.** By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1899, 28, 431—438).—A controversial paper in which the author upholds his objections to the expressions deduced by van Laar (this vol., ii, 11). A new expression is also deduced for the heat of dissociation of any electrolyte, namely,  $Q = RT^2(n-1)/(a-1) \cdot d \log k/dT$  where  $a$  is a constant introduced by the empirical dilution law,  $x^a/(1-x)v^{a-1} = k$ , obeyed by the electrolyte.  
L. M. J.

**Heat of Solution of Liquid Hydriodic Acid.** By F. G. COTTRELL (*J. Physical Chem.*, 1898, 2, 492—495).—Hydrogen iodide was prepared free from iodine by distilling from a spiral of copper wire in a closed tube, one end of which was cooled by means of solid carbonic anhydride. The heat of solution of the liquefied hydrogen iodide in water was found to be 148 Cal., and if the heat of solution of gaseous hydrogen iodide is subtracted, the latent heat of vaporisation is found to be 43 Cal.; the heat of formation of gaseous hydrogen iodide is -60 Cal., and that of the liquid is therefore -17 Cal.  
T. M. L.

**Solubility and Melting Point as Criteria for Racemic Compounds, Pseudoracemic Mixtures, and Inactive Conglomerates.** By HENDRIK W. BAKHUIS ROOZEBOOM (*Zeit. physikal. Chem.*, 1899, 28, 494—517. Compare this vol., ii, 276).—If the solubility of the two components be represented by two rectangular coordinates, then the solubility of mixtures which form an inactive conglomerate is represented by two curves  $ac$ ,  $bc$ , meeting in  $c$ , which, owing to the equal solubility of the components represents an inactive solution. Below the transition point, however, the form of the curve will be different owing to the formation of a racemic compound, and consists of three curves, those of the racemic compound and of each component, whilst at the two points of section, two solid phases occur, namely, racemic compound and one component. These points approach and ultimately coincide at the transition temperature. Hence, if evaporation go on above this temperature, one of the components first separates and ultimately the inactive mixture, and this was found to be the case by Kipping and Pope (*Trans.*, 1899, 73, 39). If, however, the racemate is stable at the temperature of evaporation, although at first either component may separate, yet the final product is a mixture of racemic compound with one component, and hence it is considered that in Kipping and Pope's experiments with potassium sodium racemate (*loc. cit.*), which do not substantiate this conclusion, the double tartrate had been formed. In the case of a partially racemic mixture, a similar result obtains, but the curves are displaced towards one or other of the axes. In a pseudoracemic mixture, the solubility curve for mixed crystals must obtain; that is, above the transition temperature the curves  $ac$ ,  $cb$  become one continuous curve, whilst below the case is similar to that of the racemic compound, but the two curves for the double solid phase become continuous. The various types of melting point curves are also considered; for a racemic compound, this must consist of three curves with two minima, and a maximum

for the inactive mixture, which, however, may be higher or lower than that of the components. For a conglomerate, the curve consists of only two parts with one minimum, and for a pseudoracemic mixture it is continuous. The melting point of a racemic compound is thus lowered by the addition of either component, that of an inactive conglomerate is raised. The author then considers the various cases which may occur owing to changes between the three types of compounds during fusion, and illustrates the cases by the possible melting point curves.

L. M. J.

**Isothermal Pressure-Surface for Two Single Salts and One Double Salt.** By FREDERICK GEORGE DONNAN (*J. Physical Chem.*, 1898, 2, 417—420).—The nature of the vapour-pressure surface for aqueous solutions of two salts, *A* and *B*, which form a single double salt, *AB*, is described. The boundary is formed by three lines, which give the vapour-pressure of the solution when saturated with regard to *A*, *AB*, and *B* respectively; on isothermal evaporation, the proportions of *A* and *B* remain unchanged until this boundary curve is reached and solid begins to separate. The composition of the solution then changes in such a way that the vapour-pressure decreases until it reaches a minimum, after which the solution remains constant in composition; such a minimum may occur at the stable quadruple points at which the solution is saturated with regard to *A* and *AB*, or *B* and *AB*, but cannot occur at any other point. A maximum may, however, occur on the part of the curve which represents the vapour pressure of solutions which are saturated with regard to *AB*; this point must be such that the constituents *A* and *B* are present in the solution in the ratio in which they combine to form *AB*, and in this case the double salt alone crystallises in a pure state from solution.

T. M. L.

**Pressure-temperature Diagrams for Binary Systems.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 1—11).—The pressure-temperature diagram for a binary system has been given by van't Hoff (*Vorlesungen über theoretische Chemie*, 35) on the assumption that the partial pressure of one of the components is negligible. The present paper contains a discussion of the various cases that are possible when neither of the partial pressures is negligible. T. M. L.

**Boiling Point Curves.** By E. F. THAYER (*J. Physical Chem.*, 1899, 3, 36—40. Compare this vol., ii, 140).—The boiling points have been determined of mixtures of alcohol and acetone, of acetone and chloroform, and of chloroform and alcohol. Mixtures of alcohol and acetone all have a boiling point intermediate between those of the separate substances. The boiling point curve for alcohol and chloroform exhibits a minimum, and a mixture containing about 7 per cent. of alcohol distils unchanged at 58.5° under 732.5 mm. pressure. The boiling point curve for chloroform and acetone exhibits a maximum, and a mixture containing about 19 per cent. of acetone distils unchanged at 63—64° under 737.1 mm. pressure.

T. M. L.

**Reversible Reactions.** By JOHN WADDELL (*J. Physical Chem.*, 1899, 3, 41—45).—In a monomolecular reaction, the form of the

differential equation which represents the velocity of change is the same whether the action is complete or incomplete. Walker and Hambly (*Trans.*, 1895, 67, 753) have assumed that it is also the case in a bimolecular reaction; this is not strictly true, and the author deduces a formula for the velocity constant in a reversible bimolecular reaction which differs in form from that which holds in a non-reversible bimolecular reaction; in the former case,  $\frac{1}{t} \log \frac{x(1 - \sqrt{a}) - A}{x(1 + \sqrt{a}) - A}$  is constant, where  $A$  is the original mass of the substance,  $x$  the mass at time  $t$ , and  $a$  is the equilibrium constant; in the latter case  $a = 1$ , and the constant is  $1/t \log A/A - x$ . T. M. L.

**Vapour Pressure of Dilute Aqueous Solutions at 0°.** By KONRAD DIETERICI (*Ann. Phys. Chem.*, 1899, [ii], 67, 859—870).—The author's determinations of the vapour pressure of solutions having been criticised by Abegg (*Abstr.*, 1898, ii, 207, 368), he has redetermined the difference between the vapour pressure of water and that of solutions of sulphuric acid, sodium chloride, cane sugar, glycerol, or carbamide at 0°, and at concentrations varying from N/1 to N/10. The accuracy of the results is discussed, and it is held that when the probable errors are allowed for, the following results are still indicated. For sulphuric acid solutions, the molecular depression of the vapour pressure does not increase with dilution between the above concentrations. In the same concentration interval, the molecular depression of sodium chloride is constant, and the determinations in both these cases are in good accord with Raoult's observations. The molecular depressions of the non-electrolytes are not equal, being greatest for dextrose and least for carbamide, results again in accord with those of Raoult and of Loomis. L. M. J.

**Freezing Point in Ternary Mixtures.** By JOHN WADDELL (*J. Physical Chem.*, 1899, 3, 160—164. Compare McIntosh, *Abstr.*, 1898, ii, 65).—The lowering of the freezing point of water by addition of acetone agrees well with that calculated for a molecular depression of 18.5. The addition of a third substance, slightly miscible with water and readily miscible with acetone, might be expected in some cases to lower the freezing point until a certain quantity had been added, and then cause a rise in the freezing point. The addition of salicylic acid, phenol, paranitrophenol, or quinol was found to give a steady rise in the freezing point; in the last case, however, the addition of 0.755 gram to a solution of 9.71 grams of acetone in 100 grams of water caused no rise in the freezing point, and it is possible that a smaller quantity of quinol might have caused an initial depression. Ether causes a steady depression of the freezing point, and no subsequent rise could be observed. T. M. L.

**Internal Friction of Gases and its Alteration with Temperature.** By PAUL BREITENBACH (*Ann. Phys. Chem.*, 1899, [ii], 67, 803—827).—Determinations of the internal friction of air, ethylene, hydrogen, carbonic anhydride, and methylic chloride were made, by the transpiration method, at a series of temperatures varying between -20 and 300°. The viscosity is proportional to the absolute tem-

perature raised to a fractional power, that is  $\eta \propto T^x$ ; the value of  $x$  differs, however, for different gases, varying between 0.6 and 1.0 for the five gases examined, but remains *approximately* constant for each gas through the whole range of temperature, although the change is always a decrease for the higher temperatures. For mixtures of gases, an additive law is not obeyed, the viscosity of a mixture of carbonic anhydride and hydrogen being greater, and that of ethylene and air less, than that calculated from the percentage composition. Experiments were also made to determine the sliding of the air over the glass surface, an effect which, in Schumann's opinion, rendered the transpiration method inaccurate at high temperatures. This was, however, found to be extremely slight, and to vary but slightly with temperature, so that Schumann's objection does not hold. L. M. J.

**Mixtures of Gases and their Compressibility.** By DANIEL BERTHELOT and PAUL SACERDOTE (*Compt. rend.*, 1899, 128, 820—822).—The authors have determined the value of  $A$  in the expression  $P_1V_1/P_2V_2 - 1 = A(P_2 - P_1)$  at  $16^\circ$  and between 1 and 2 atmospheres for certain mixtures of gases, with the following results:

	Value of $A$ .
Carbonic anhydride, 505 vols., and sulphurous anhydride, 495 vols. ....	$143 \times 10^{-6}$
Air .....	$5 \times 10^{-6}$
Hydrogen and oxygen, equal volumes.....	$-2 \times 10^{-6}$

In the cases of carbonic anhydride and sulphurous anhydride and of oxygen and hydrogen, the observed value is distinctly lower than that calculated; in the case of air, the difference between the two values is not greater than the error of experiment. The mixture by diffusion of equal volumes of oxygen and hydrogen is accompanied by an increase of pressure of 0.20 mm. C. H. B.

**Kinetic Theory of Liquids.** By GUSTAV JÄGER (*Ann. Phys. Chem.*, 1899, 67, 894—898).—A reply to some criticisms of Voigt and Dieterici on the author's many deductions, based on the application of the kinetic theory to liquids, which have appeared in numerous papers in the *Wiener Sitzungsberichte* from 1890. L. M. J.

**An Equation Representing the Molecular Weight of Liquids in Terms of their Densities and Critical Constants.** By DANIEL BERTHELOT (*Compt. rend.*, 1899, 128, 606—609).—Young proved experimentally that, for any fluid at the critical temperature, there is a constant ratio between the critical volume and the theoretical volume calculated from the law of perfect gases. The constant being taken as  $1/3.6$ , the relationship between the molecular weight and the critical constants is represented by the equation  $M = 22.4.T_c d_c / 3.6 \times 273.p_c$ . Mathias showed that, providing the temperature is sufficiently remote from the critical, the following relationship is approximately true:  $d_c = d/2(2 - T/T_c)$ , where  $d$  is the density of a liquid at the absolute temperature  $T$ .

On eliminating  $d_c$  from these equations, a third expression,  $M = 11.4.T_c d/p_c(2 - T/T_c)$ , is obtained, by means of which the value of

the molecular weight in the liquid state may be calculated. A table is given comparing the values obtained from the equation with those deduced from the chemical formulæ; it indicates that, in the great majority of cases, the substance, whether elementary or compound, has the same molecular complexity in the liquid as in the gaseous state. Water and the aliphatic acids and alcohols alone show signs of polymerisation.

G. T. M.

**Influence of an Electrolyte of Two Ions on the Solubility of an Electrolyte of Three Ions.** By ARTHUR A. NOYES and EDWARD S. CHAPIN (*Zeit. physikal. Chem.*, 1899, 28, 518—522).—The expressions for indicating the influence of an electrolyte of two ions on the solubility of an electrolyte of three ions are deduced and simplified for the case where one of the compounds is but slightly soluble and one of the products but slightly dissociated. The solubility of calcium hydroxide in solutions of ammonium chloride was found to give results in accord with the calculated expressions (compare this vol., ii, 9, 274).

L. M. J.

**Determination of Solubility at different Temperatures.** By BRONISLAW PAWLEWSKI (*Ber.*, 1899, 32, 1040—1041).—In preparing a saturated solution, air is drawn through the liquid by a glass tube bound round at the bottom with linen; when the solution is saturated, the direction of the air current is reversed and the solution driven back through the tube into a weighed vessel. By immersing the whole apparatus in a beaker full of water, the solubility can be determined at any temperature. A sketch of the apparatus is given in the paper, and also a table showing the solubility of potassium chlorate in water for every 5 degrees from 0° to 100°.

T. M. L.

**Solid Solutions.** By HAMILTON P. CADY (*J. Physical Chem.*, 1899, 3, 127—136).—Naphthalene and monochloroacetic acid form one series of liquid, but two of solid, solutions. The freezing points of liquid mixtures, in varying proportions, have been determined, and plotted as a curve, the eutectic point being 53° for a liquid mixture of 28·7 parts of naphthalene and 71·3 parts of the acid. The solubility of naphthalene in the solid acid is limited to 2·5 parts in 100 of the mixture, and that of the acid in solid naphthalene to 57 parts in 100 parts of the mixture; mixtures of intermediate composition deposit two kinds of crystals on cooling after fusion. Glycollic acid also forms two series of solid solutions with naphthalene, and dissolves in it to a larger extent than chloroacetic acid; acetic acid, and probably also malonic and succinic acids, do not form solid solutions with naphthalene. The depression of the freezing point in cases where a solid solution separates cannot be calculated from the van't Hoff-Raoult formula, and usually  $n/N$  is less than  $\log p/p_1$  for the solid solution. The author regards the discrepancy as due to thermal effects, such as the presence of a noticeable heat of dilution in the solid solution.

T. M. L.

**Solution Densities.** By H. T. BARNES and A. P. SCOTT (*J. Physical Chem.*, 1898, 2, 536—550).—The authors have determined the densities at different concentrations of solutions of sulphuric acid and

zinc, magnesium, cadmium, potassium, and sodium sulphates, hydrochloric acid, and sodium and potassium chlorides, and magnesium, zinc, potassium, and sodium nitrates. The results are given in tables, and are also plotted in the form of curves which show the relationship between the concentration of the solution and the difference between the observed density and that calculated on the assumption that no increase of volume occurs on adding the salt to the water. The relatively abrupt break in the curve, observed in the case of zinc sulphate (Callendar and Barnes, *Abstr.*, 1898, ii, 276), appears in a less marked degree in the curves for magnesium sulphate and cadmium sulphate, but is not noticeable in the other cases investigated.

T. M. L.

**Demonstration of the Phase Rule.** By PAUL SAUREL (*J. Physical Chem.*, 1899, 3, 69—71, and 137—143).—Two mathematical papers, unsuitable for abstracting.

T. M. L.

**Equilibrium in Systems of Two and Three Components with a Liquid Phase.** By GIUSEPPE BRUNI (*Gazzetta*, 1898, 28, ii, 508—529).—The author has compared the saturation phenomena of the different cases of binary mixtures with the corresponding equilibrium phenomena of ternary mixtures, confining himself to systems with only one liquid phase. The ternary mixtures were obtained by adding to the binary mixture, in the form of a solvent, a third substance, which does not combine, and is not isomorphous, with the primitive components; to the cryohydric solution (containing undissolved crystals) of each component in this solvent were added increasing quantities of the other component until the solution became saturated with both, the temperature corresponding with the double cryohydric point being then read off. There are four cases: 1. The components of the binary mixture do not form an additive compound and are not isomorphous. An example is found in mixtures of naphthalene and diphenylamine, which were studied by Roloff (*Abstr.*, 1895, ii, 438). The corresponding ternary system, benzene, naphthalene, and diphenylamine, was examined by the author. 2. The two components form an additive compound (stable) which separates without decomposition at the freezing point. Picric acid and  $\beta$ -naphthol, investigated by Kuriloff (*Abstr.*, 1897, ii, 397), come under this head. For the ternary system, the author used ethylenic bromide as solvent. 3. The two components form an additive compound (unstable) which decomposes on separating from solution. No example of this class was investigated. 4. The two components are isomorphous. The systems (*a*) benzene, naphthalene,  $\beta$ -naphthol, and (*b*) benzene, phenanthrene, carbazole, corresponding with the binary systems examined by Küster (*Abstr.*, 1895, ii, 439) and Garelli (*Abstr.*, 1895, ii, 206) respectively were studied; in both of these cases, it was noticed that, the solidifying point of the solution was raised on adding increasing quantities of the less soluble component ( $\beta$ -naphthol or carbazole) to the cryohydric solution of the more soluble component (naphthalene and phenanthrene respectively). This behaviour is strictly analogous to that of the two binary mixtures.

The results show that if to a system of two components with one,



and only one, possible liquid phase there be added a third component which does not combine with the first two and is not isomorphous with them, the curves expressing equilibrium of the same order (saturation curve in the binary system and cryohydric curve in the ternary system) are similar, the only difference being that, in systems represented by curves of ternary mixtures, there is one more solid phase. T. H. P.

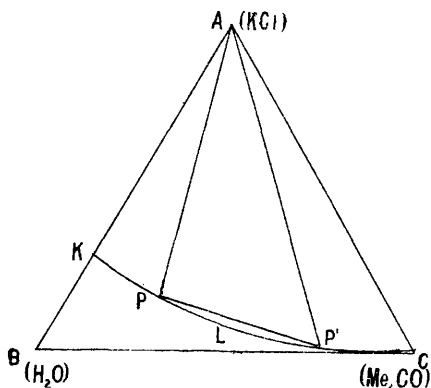
**Physical Equilibrium of Isomorphous Mixtures.** By GIUSEPPE BRUNI (*Gazzetta*, 1899, 29, i, 149—151).—The author brings forward evidence in addition to that already adduced by him to show the general inapplicability of Küster's second law regarding the physical equilibrium of isomorphous mixtures, namely, that for mixtures of substances perfectly isomorphous the solid phase separating during the freezing has the same composition as the liquid. This law only holds in one particular case, that is, when the freezing point curve for a given pressure runs parallel to the axis of concentrations, or when the two components of the mixture have the same freezing point.

T. H. P.

**Potassium Chloride in Aqueous Acetone.** By J. F. SNELL (*J. Physical Chem.*, 1898, 2, 457—491).—The author discusses the nature of the equilibrium in the system potassium chloride—water—acetone, which is capable under certain conditions of giving two liquid phases. At temperatures at which separation occurs, the triangular isothermal diagram for the system will in general have the form shown in the figure. Here  $A = \text{KCl}$ ,  $B = \text{water}$ ,  $C = \text{acetone}$ ; the curve  $KPP'C$  shows the solubility of potassium chloride in mixtures

of acetone and water, the solubility in pure water being shown at  $K$  and the solubility in acetone being very slight; two liquid phases occur in mixtures in which the components are present in proportions represented by points lying within  $APLP'A$ . Thus  $BKLCB$  represents one liquid phase in equilibrium with vapour,  $PLP'P$  represents two liquid phases in equilibrium with vapour,  $APP'A$  represents two liquid phases in equilibrium with solid and vapour,  $AKPA$  and  $ACP'A$  represent each a liquid phase (consisting chiefly of water and acetone respectively) in equilibrium with solid and vapour.

For all points within  $APP'A$  the composition of the two liquid phases will be represented by  $P$  and  $P'$ , but for points within  $PLP'P$  by two conjugate points on  $PLP'$ , which become identical and vanish at the point  $L$ . If an axis of temperature be introduced perpendicularly to the paper, the line  $PLP'$  will become the trace of a surface, to which the name of 'dimeric surface' is applied, the area  $PLP'P$  becomes the



trace of the '*dineric space*,' and the area  $APP'A$  the trace of the '*stereo-dineric space*.' In systems of the type studied in this paper, only one liquid phase is possible at lower temperatures, and with decreasing temperature the points  $PLP'$  approach each other until they become coincident and vanish at a point  $\sigma$ , the '*plait point*' of the surface. Thus the dineric surface appears as an excrescence on the solubility surface (of which  $KC$  is the trace), which becomes more pronounced as the temperature rises, the points  $PP'$  of the boundary curve becoming more divergent, and the '*crest-curve*,' of which  $L$  is the trace, becoming more elevated. If the miscibility of the two liquid components decreases with falling temperature, a second dineric surface may appear, the plait point in this case representing a maximum, and not a minimum, temperature for the formation of two layers; such a maximum has been observed in the case of sodium chloride, water, and succinonitrile, but the upper dineric curve did not appear even when the temperature was raised to the point of decomposition, (Schreinemakers, Abstr., 1897, ii, 483).

In the system acetone—water—potassium chloride, the plait point  $\sigma$  lies in the isothermal plane of  $32.5^\circ$  and corresponds with the composition  $H_2O : COMe_2 : KCl = 43 : 50 : 7$ . The isotherm of  $30^\circ$  is therefore found to give a continuous solubility curve  $KC$ . In the isotherm of  $40^\circ$ , the solubility curve is intersected by the dineric curve at  $P$  and  $P'$ , corresponding with  $H_2O : COMe_2 : KCl = 59.0 : 25.2 : 15.8$  and  $23.7 : 74.9 : 1.4$ ; this is the isotherm represented in the figure. The isotherm of  $50^\circ$  has also been plotted.

For systems of the type salt—water—organic liquid, it is usually found that the dineric surface overhangs the boundary line,  $P$  and  $P'$ , so that within certain limits an unsaturated solution is found to separate into two layers on raising the temperature. The minimum temperature at which separation occurs has been determined for about 50 solutions, and gives a corresponding number of points on the dineric surface; the temperatures of separation of saturated mixtures of water and acetone in different proportions have also been determined and plotted in the form of a curve, which thus forms a projection of the boundary curve of the dineric surface, the minimum point being the projection of the plait point of the system. Theoretically, the line of constant composition should cut the dineric surface again on a higher temperature, and the two liquid phases should again become one, but actually this has not been observed in the case under consideration; in a mixture of water (66.4 parts), alcohol (16.8 parts), and potassium carbonate (16.8 parts), however, the two liquid phases which appear at  $40^\circ$  disappear again at  $70^\circ$ , as required by the theory. In the system naphthalene—acetone—water, Cady (this vol., ii, 82) found that it was not possible to obtain an unsaturated solution which would separate into two layers on heating; in this case therefore the dineric surface does not overhang the boundary curve. T. M. L.

**Alcohol Water and Potassium Nitrate.** By NORMAN DODGE and L. C. GRATTON (*J. Physical Chem.*, 1898, 2, 498—501. Compare preceding abstract).—The temperatures have been determined at which mixtures of alcohol and water in different proportions will

separate into two layers in presence of an excess of potassium nitrate. The minimum temperature at which separation will take place is  $80^{\circ}$  in a mixture containing about 39 per cent. by weight of alcohol. The addition of a second salt facilitates the formation of two layers; thus separation occurs in a 35 per cent. solution at  $80^{\circ}$  in presence of an excess of potassium nitrate, but at  $65^{\circ}$  in presence of potassium nitrate and chloride, although potassium chloride alone does not cause any separation even at  $140^{\circ}$ .

T. M. L.

**Absorption of Water Vapour by Compounds and its Partition between two Similar and two Dissimilar Substances.** By W. J. BUSNIKOFF (*Chem. Centr.*, 1898, ii, 745—746; from *J. Russ. Chem. Soc.*, 30, 418—429. Compare this vol., ii, 360).—Sodium chloride, placed in a desiccator containing water, had in 55—61.9 days absorbed enough water to dissolve it, forming a hydrate of a composition between that of  $\text{NaCl} + 8.61\text{H}_2\text{O}$  and  $\text{NaCl} + 9.85\text{H}_2\text{O}$ ; when this solution was placed over sulphuric acid, crystals began to separate as soon as its composition became  $\text{NaCl} + 9.16\text{H}_2\text{O}$ , and a solution containing  $\text{NaCl} + 9.495\text{H}_2\text{O}$  deposited crystals immediately it was placed over the acid, hence the critical hydrate is  $\text{NaCl} + 9.5\text{H}_2\text{O}$ . When a solution,  $\text{NaCl} + 19\text{H}_2\text{O}$ , containing 1.8564 grams of the chloride, and 8.6004 grams of 93.82 per cent. sulphuric acid were placed under the same vessel, the former had lost all its water after 29.1 days, whilst the composition of the latter was  $\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$ . The curve of the velocity of absorption of water vapour by sodium chloride shows the same regularity as those for sulphuric acid and calcium chloride.

The critical hydrate of barium chloride is  $\text{BaCl}_2 + 3\text{H}_2\text{O}$ , and the absorption curve is almost a straight line deviating a little towards the abscissæ axis. When a solution of the composition,  $\text{BaCl}_2 + 31.86\text{H}_2\text{O}$ , containing 4.0080 grams of water was placed under the same vessel with 3.3293 grams of  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , the solutions had, in 36 days, become  $\text{BaCl}_2 + 2.08\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 + 5.031\text{H}_2\text{O}$  respectively, hence the affinities of the hydrates  $\text{BaCl}_2 + 2\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}$  for water are the same. When this solution of barium chloride was again placed with 7.057 grams of sulphuric acid containing 6.6449 of  $\text{H}_2\text{SO}_4$ , equilibrium was attained in 58.9 days, and the solutions had the composition  $\text{BaCl}_2 + 0.958\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 + 1.026\text{H}_2\text{O}$  respectively. Experiments showed that the hydrate  $\text{BaCl}_2 + \text{H}_2\text{O}$  is not as hygroscopic as  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ .

A solution containing 2.1848 grams of magnesium chloride in 1.8818 of water ( $\text{MgCl}_2 + 4.56\text{H}_2\text{O}$ ), after remaining over water for 166 days, had attained the composition  $\text{MgCl}_2 + 17.37\text{H}_2\text{O}$ , and the absorption curve up to  $\text{MgCl}_2 + 9.33\text{H}_2\text{O}$  is nearly straight. This solution of magnesium chloride, when placed in the same vessel with 14.1988 grams of a solution of sulphuric acid containing 13.1988 of  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , changed to an ice-like mass when its composition was  $\text{MgCl}_2 + 7.13\text{H}_2\text{O}$ , and then gradually formed a white solid; in 34.9 days, the solutions had the composition  $\text{MgCl}_2 + 6.944\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 + 2.185\text{H}_2\text{O}$  respectively, and finally, after renewing the

sulphuric acid, equilibrium between the hydrates  $\text{MgCl}_2 + 3.5\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  was established.

E. W. W.

**Reciprocal Salt Pairs. II. Equilibrium Phenomena in the Presence of a Double Salt.** By WILHELM MEYERHOFFER and A. P. SAUNDERS (*Zeit. physikal. Chem.*, 1899, 28, 453—493. Compare Abstr., 1896, ii, 414).—The reciprocal salt pair sodium sulphate | potassium chloride is investigated; for this pair, at  $3.7^\circ$  a transition occurs with formation of the double salt  $\text{K}_3\text{Na}(\text{SO}_4)_2$  and sodium chloride, whilst, further, at  $32.4^\circ$  there occurs the change from hydrated to anhydrous sodium sulphate. Representing the hydrated sodium sulphate by  $G$ , and the double salt by  $D$ , the author finds that below  $4.4^\circ$  the triad phases (1)  $G$ ,  $\text{NaCl} + \text{KCl}$ , and (2)  $G$ ,  $\text{KCl} + D$  are stable, and above this temperature (3)  $D$ ,  $\text{NaCl} + \text{KCl}$  and (4)  $D$ ,  $\text{NaCl} + G$ , and it is noteworthy that in none of these does  $\text{K}_2\text{SO}_4$  occur. Below  $-14^\circ$ , however, the triad  $G$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$  occurs as a solid phase changing at this temperature to either (2) or (5)  $\text{K}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $D$ , the former being one of the triad phases of the  $4.4^\circ$  transition group. The possibility of  $\text{K}_2\text{SO}_4$ ,  $\text{NaCl}$  coexisting occurs if the saturation curves of (3) and (5) cut. Further investigations at higher temperatures were therefore undertaken, and the apparatus used is described and includes a new form of pipette for the determination of the density of saturated solutions. For the determination of the compounds present in the solid phases, the authors indicate a method which consists in the application of certain characteristic inequalities to the results of the analysis. Thus, for the group (3) the characteristics are  $\text{Na}_2 > \text{SO}_4 \mid 4$  and  $\text{K}_2 > 3\text{SO}_4 \mid 4$ , &c. The complete solubility diagrams are given for the isotherms of  $0^\circ$ ,  $4.4^\circ$ ,  $16.3^\circ$ , and  $25^\circ$ . From these, it is evident that the second transition point at which sodium chloride and potassium sulphate coexist is at any rate far above  $25^\circ$ . The observations of Mazotto (Abstr., 1891, 388) and of Precht and Wittgen (Abstr., 1882, 1264) on the solubility of mixtures of sulphates and chlorides of potassium and sodium are also examined and are shown to be, for the most part, in accord with the authors' experiments.

L. M. J.

**The Conversion of Ammonium Thiocyanate into Thiourea [Thiocarbamide] and of Thiourea into Thiocyanate.** By JOHN WADDELL (*J. Physical Chem.*, 1898, 2, 525—535).—The conversion of ammonium thiocyanate into thiocarbamide, and *vice versa*, is a monomolecular reaction, similar to the case of the two hexachloroketocyclopentenes studied by Küster (Abstr., 1896, ii, 158). Solid ammonium thiocyanate was not changed when heated at  $93^\circ$  for 8 hours a day during 8 months, and only a small quantity of thiocarbamide was produced by boiling the aqueous solution at  $109^\circ$  during 50 hours. The thiocarbamide was estimated by titration with ammoniacal silver nitrate, which gives silver sulphide and cyanamide, and the ammonium thiocyanate by titration with silver nitrate. Equilibrium is reached at  $152^\circ$  when the thiocarbamide and ammonium thiocyanate are present in the ratio of 21.2 to 78.8. The velocity constant, which represents the total weight of substance which would undergo isomeric

change on heating one gram of each isomeride during one minute, was found to be 0.00649 and 0.00645 in the conversion of ammonium thiocyanate into thiocarbamide, and 0.00622 in the conversion of thiocarbamide into thiocyanate at 152—153°; the constants should of course be the same, but the agreement noticed here is only rarely observed, owing to the presence of disturbing secondary actions. At 160—161°, the constant was 0.0145 for the conversion of thiocyanate into thiocarbamide, and 0.0123 for the conversion of thiocarbamide into thiocyanate, the velocity of change being doubled by a rise of 8° in the temperature.

T. M. L.

**Dissociation Studies. I.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 72—94).—A discussion of the equilibrium between a dissociating substance and two products of dissociation on the basis of Duhem's theory of permanent changes (Abstr., 1897, ii, 439), similar to that recently given for the equilibria between two dynamic isomerides (this vol., ii, 145). The theory is applied to the cases of phthalic and succinic acids (formation of anhydride), chloral hydrate and alcoholates, and aldehyde ammonia, which have been examined experimentally by Ramsay and Young (*Phil. Trans.*, 1886, 177, i, 82).

T. M. L.

**Benzaldoxime.** By FRANK K. CAMERON (*J. Physical Chem.*, 1898, 2, 409—416).—Bancroft's theoretical conclusions on the equilibria of stereoisomerides (this vol., ii, 145) are applied to the melting point phenomena of benzaldoxime, and it is shown that the double melting point curve can be realised experimentally. The stable  $\alpha$ -form melts at 34—35°, and the labile  $\beta$ -form at 130°; the stable triple point at which the solid  $\alpha$ -modification is in equilibrium with the liquid mixture and with the vapour phase, Duhem's 'natural melting point,' is 27.7°, and the eutectic point is 25—26°. The equilibrium between the  $\alpha$ - and  $\beta$ -forms is independent of the temperature, and is reached when there is about 6 per cent. of the  $\beta$ -form in the liquid mixture; at the eutectic point, the liquid mixture contains 9 per cent. of the  $\beta$ -form. By repeated fusion, the melting point of the  $\beta$ -form fell from 130° to 114°, 98°, 76°, and finally to 26°, corresponding with a gradual change in the composition of the mixture. The freezing points of mixtures of the  $\alpha$ - and  $\beta$ -forms in various proportions were determined and plotted in the form of a curve, which consisted of two intersecting straight lines, equally inclined to the vertical; the molecular depression of the freezing point is therefore the same for both isomerides. The molecular heats of fusion are calculated to be 14.3 for the  $\beta$ -, and 8.3 for the  $\alpha$ -form.

T. M. L.

**Equilibria of Stereoisomerides. III.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 144—155. Compare this vol., ii, 145).—The effects are discussed of adding to a mixture of two dynamic isomerides a third substance which forms a compound with one or both of the isodynamic forms. The theory is applied to the formation of two hydrochlorides and two sodium salts from  $\alpha$ - and  $\beta$ -benzaldoxime and from some of its substitution products, a reversal of stability occurring in the formation of the hydrochlorides. The equilibrium between fumaric and maleic acids in presence of ammonia and between chloral

and metachloral in presence of water are also given as examples of the application of the theory.

T. M. L.

**Distance of Action of Molecular Forces.** By WILHELM MÜLLER-ERZBACH (*Ann. Phys. Chem.*, 1899, [ii], 67, 899—890).—Determinations have been made of the thickness of layers of gum required to protect wax or sealing-wax from the action of carbon bisulphide; the values obtained are about 0.1 mm., but are different for the two substances.

L. M. J.

**Explosion of Acetylene when mixed with Inert Gases.** By MARCELLIN P. E. BERTHELOT and PAUL VIEILLE (*Compt. rend.*, 1899, 128, 777—787).—The authors have made experiments on the explosibility of mixtures of acetylene with various proportions of hydrogen or coal gas, with a view to ascertain the limits of pressure below which the decomposition is not propagated throughout the mass of the gas. The results are given in tabular form, and as a rule there is considerable difference between the observed and calculated pressures, the differences being due either to the slow rate at which decomposition takes place, or to the fact that it is incomplete.

The pressure at which propagation of the decomposition under the influence of an incandescent wire ceases to take place is higher the smaller the proportion of acetylene, but rapidly approximates to the limit for pure acetylene as the proportion of this gas is increased. It was not found possible to determine for each mixture an exact critical pressure below which explosion will not take place, but the experiments show that there is in each case a certain range of pressure within which the probability of the propagation of explosion varies very rapidly, but below which the probability is extremely small.

With mixtures of equal volumes of acetylene and hydrogen, the limiting pressure is about 4 kilos. per square cm.; with 2 volumes of hydrogen and 1 of acetylene, it is about 7 kilos., and with 3 volumes of hydrogen, about 10 kilos. With corresponding mixtures of acetylene and coal gas, the values are about 7 kilos., 12 kilos., and 40 kilos. respectively. These values will be lower, especially at low pressures, the larger the volume of the gas, and consequently the smaller the cooling influence of the walls of the vessel.

The limits at which the probability of propagation of the decomposition becomes  $1/2$  are somewhat higher in each case, but not much higher than those specified. The greater influence of coal gas as compared with hydrogen is to be attributed to the presence of a large proportion of methane, the decomposition of which would necessitate a considerable absorption of heat.

C. H. B.

**Principle of Maximum Work.** By DONATO TOMMASI (*Bull. Soc. Chim.*, 1898, [iii], 19, 439—441).—When a solution containing copper and silver nitrates is electrolysed, the latter salt does not undergo decomposition until the atomic proportions of copper and silver present in the solution are as 15 to 1; when the ratio becomes 87 to 2, the product of electrolysis consists of copper and silver in atomic proportion (1 : 1). According to the principle of maximum work, the whole of the silver should be precipitated before the copper nitrate begins to decompose.

A solution of potassium chlorate, when electrolysed, ought to undergo reduction rather than oxidation, according to this principle, since the former reaction,  $\text{KClO}_3 + 3\text{H}_2 = \text{KCl} + 3\text{H}_2\text{O}$ , generates 224.4 Cal., whereas the latter,  $\text{KClO}_3 + \text{O} = \text{KClO}_4$ , only liberates 17.6 Cal. As a matter of fact, it is the latter reaction which takes place.

An acidified solution of hydrogen peroxide, when electrolysed, evolves hydrogen, due to the decomposition of the water, but the peroxide is not reduced, although its reduction would be accompanied by a development of heat. If a solution of copper sulphate and hydrogen peroxide is placed in contact with the platinum anode of a voltaic cell and the circuit completed, copper is deposited, but the peroxide remains unaltered.

From these observations, the following generalisations are deduced:—(1) If a substance is treated in such a manner that it can react in one of two ways, the more exothermic reaction will occur, provided that this is capable of being started. (2) When two modes of action are possible, that reaction will take place which requires less energy to start it, although it may be less exothermic than the other.

The author proposes to replace the above-mentioned principle by another—the principle of minimum work—which may be enunciated in the following manner: Whatever be the amount of heat generated or absorbed during the course of a chemical change, the reaction which can be started with the least expenditure of energy will take place by preference.

G. T. M.

**New Compressed Air Pump.** By PAUL BOURCET and G. BERLEMONT (*Bull. Soc. Chim.*, 1898, 19, [iii], 479).—The lower portion of a filter pump is fitted into the central stopper of a three-necked Woulf's bottle; the upper portion is attached to a water tap. The Woulf's bottle is also fitted with an outlet tube for delivering the compressed air, and a syphon so regulated that one-third of the bottle remains filled with water when the pump is working.

G. T. M.

**Hydrogen Sulphide Generator.** By WALTER P. BRADLEY (*Amer. Chem. J.*, 1899, 21, 370–376).—The apparatus consists of three glass bottles, A, B, and C, each provided with an orifice near the bottom. The generator proper, A, has a capacity of about 16 litres, and should never be less than half full of large pieces of ferrous sulphide; it is not connected directly with the acid reservoir, B (8 litres), but indirectly by means of the third bottle, C, which serves as a gas reservoir, and has a capacity of about 4 litres; B and C are connected by the lower tubulures. The connection between C and A is by a tube which just passes through the top orifice in each and terminates in A as a fine capillary.

The acid reservoir may be fixed permanently at a convenient height above A, or may be so arranged that its height can be varied according to the pressure to be overcome. When gas is being drawn off from A, a small quantity of acid flows in through the capillary tube on to the sulphide; when the demand ceases, the gas formed accumulates in C; on renewed demand for gas, first the accumulated gas, then

fresh acid, passes from C into A. The advantage of the method is that the acid remains in contact with the iron sulphide until it is spent and can then be removed by the lower orifice in A. J. J. S.

[Apparatus similar in principle have been in use in the laboratories of the Mason University College and the Central Technical College for some years.—EDITOR.]

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## Inorganic Chemistry.

**New Explosive and Detonating Materials.** By UGO ALVISI (*Gazzetta*, 1899, 29, i, 121—143).—The author claims priority in the preparation of explosives containing ammonium perchlorate as their principal constituent. By using this salt in place of the other oxidising components of explosives, or by adding it to such explosives as contain enough oxygen for their combustion, an increase is obtained both in the ballistic and in the disruptive power. Also the ratio of the disruptive to the ballistic power has a higher value, which makes these explosives of especial use in mines.

Mixtures of ammonium perchlorate with carbon and with carbon and sulphur give good results as regards their hygroscopic properties, resistance to shock, keeping quality, &c. T. H. P.

**Action of Hydrogen Peroxide on Halogen Oxy-acids.** By SIMEON M. TANATAR (*Ber.*, 1899, 32, 1013—1015).—Hydrogen peroxide has no action on perchloric or chloric acids in alkaline or in acid solution. Periodic acid is reduced to iodic acid in alkaline or acid solution, but the iodic acid is stable. Bromic acid is reduced to hydrogen bromide, together with a little bromine, since hydrogen bromide is oxidised by hydrogen peroxide. T. M. L.

**Absence of Free Iodine and Gaseous Iodides in the Atmosphere of Toulouse.** By F. GARRIGOU (*Compt. rend.*, 1899, 128, 884—885).—A large volume of air from this town was filtered through cotton wool and aspirated through a solution of pure caustic potash; the residue obtained on evaporating the solution was treated with alcohol, and the extract, after distilling off the solvent, left a slight deposit which, on treatment with dilute sulphuric acid, zinc nitrite, and starch solution, proved to be free from iodides.

The steam evolved from the brine pans of Salies-de-Béarn, contains a notable quantity of sodium chloride, but no trace of iodides.

G. T. M.

**Machines for the Manufacture of Liquid Air.** By CARL LINDE (*Ber.*, 1899, 32, 925—927).—The author points out that numerous proposals have been made at various times to produce a cumulative cooling effect by allowing a compressed gas to expand and thus cool a further quantity of the compressed gas. He claims to have been the first to utilise the Thomson-Joule effect for the production of cold in this way, and points out that Ramsay (*Ber.*, 1898, 31, 3116) is in error in ascribing an earlier use of this principle to Hampson. A. H.

**Molecular Weight of Sulphur.** By SAMUEL D. GLOSS (*J. Physical Chem.*, 1898, 2, 421—426. Compare Abstr., 1888, 1027; 1889, 673; 1890, 447, 1043; 1891, 260; 1896, ii, 357).—The molecular weights of monoclinic, rhombic, and plastic sulphur have been determined by the freezing point method in solution in naphthalene and in phosphorus, care being taken to avoid heating much above the melting point. For concentrations of 1 or 2 per cent. in naphthalene solutions, the values found were  $M=287$  and  $271$  for rhombic,  $283$  for plastic, and  $293$  for monoclinic, no marked differences being observed between the three varieties. The addition of 11 per cent. of sulphur to phosphorus brought the melting point down to  $27^\circ$ , and gave the values  $M=259$  for rhombic, and  $260$  for monoclinic sulphur; a further addition of 3 per cent. gave  $M=317$  for rhombic,  $311$  for monoclinic, and  $329$  for plastic sulphur; these values are higher than those obtained for an 11 per cent. solution, but are chiefly important as showing that no difference in molecular weight can be detected between the three forms, even when the temperature is kept below  $27^\circ$ .

T. M. L.

**Molecular Weight of Sulphur in Carbon Bisulphide Solutions.** By H. T. BARNES (*J. Physical Chem.*, 1899, 3, 156—159. Compare this vol., ii, 405).—From Pfeiffer's density determinations (Abstr., 1897, ii, 488), the number of molecules of solvent that are displaced by a molecule of sulphur is calculated, and it is shown that  $S_4$  and  $CS_2$  have approximately the same molecular volume; it is therefore concluded that the molecule of sulphur has the formula  $S_{4n}$ , where the magnitude of  $n$  depends on the complexity of the molecule of carbon bisulphide.

T. M. L.

**Combination of Sulphur with Hydrogen.** By DMITRI P. KONOWALOFF (*Chem. Centr.*, 1898, ii, 657; from *J. Russ. Chem. Soc.*, 1898, 30, 371—374).—The author finds that the results of his work on the combination of trimethylethylene with acids (Abstr., 1888, 1167) do not agree with Duhem's theory (*Traité élémentaire de mécanique chimique fondée sur la thermodynamique*) and Pélabon's data (Abstr., 1897, ii, 312), which show that the combination of sulphur and hydrogen at  $215$ — $350^\circ$  reaches a limit which is not dependent on the reverse change, for hydrogen sulphide is not decomposed at these temperatures. According to the author, however, although hydrogen sulphide is not decomposed at  $310^\circ$ , there is no limit to the combination of hydrogen and sulphur at this temperature.

E. W. W.

**Hydroxylamine.** By SIMEON M. TANATAR (*Ber.*, 1899, 32, 1016. Compare this vol., ii, 285).—The product obtained by the action of sulphurous acid on hydroxylamine was pure ammonium sulphate, and not sulphamic acid, although this is evidently the first product of the action. In reply to Brühl, it is stated that the similarity of behaviour between hydroxylamine and hydrogen peroxide does not necessarily imply similarity of structure.

T. M. L.

**The Heteromorphic (Allotropic) Modifications of Phosphorus and Arsenic, and of Ferrous Sulphide.** By GOTTLIEB ED. LINCK (*Ber.*, 1899, 32, 881—897).—The term *eutropic* is applied to any

series formed by the combination of the successive elements of a subgroup of the elements in the natural system with the same radicle, when the compounds thus produced are characterised by similar crystalline form and similar physical and chemical constants, which, however, show a progressive change with the change in molecular weight. The *crystal-volume* of a substance can be calculated from the geometrical constants of its crystals (Linck, *Zeit. Kryst. Min.*, 1896, 26, 280), and it has been found that the true molecular volume stands in a simple integral proportion to this calculated crystal-volume. It further follows from this that the relative weights of the crystal molecules of allotropic substances also stand to one another in a simple ratio.

Red phosphorus crystallises in rhombohedra of the hexagonal system, but this form is not eutropic with the ordinary rhombohedral forms of arsenic, antimony, and bismuth, because the properties of rhombohedral phosphorus, such as the calculated ratio of the axes, the atomic volume, behaviour towards oxygen, &c., do not fit into the eutropic series formed by the other three elements. On the other hand, red phosphorus appears to form a eutropic series with mirror arsenic, which has a sp. gr. 4.71, is transparent in thin films, and passes into the ordinary crystalline form of arsenic at 358—360°. Finally, ordinary yellow phosphorus corresponds eutropically with the yellow modification of arsenic. The latter is best obtained by gently heating arsenic in a current of carbonic anhydride and strongly cooling the tube, which must not be exposed to light; under these circumstances, a yellow powder is deposited, which is converted into the mirror form of arsenic by heat or exposure to light. This yellow powder is readily soluble in carbon bisulphide, and by evaporating the solvent is deposited in microscopic, rhombic dodecahedra which smell strongly of garlic. These change spontaneously into mirror arsenic, and the transformation, which can be watched under the microscope, is complete in about 3 minutes. No corresponding form of antimony or bismuth is known, whilst the ordinary opaque rhombohedral form of arsenic corresponds eutropically with crystalline antimony and bismuth, no form of phosphorus corresponding with these being known.

No definite difference in composition has been established between magnetic pyrites and artificial ferrous sulphide on the one hand, and troilite on the other. The first two crystallise in forms belonging to the hexagonal system, whilst troilite is stated to belong to the regular system. Troilite, however, cannot be a heteromorphic form of magnetic pyrites, because the weights of the crystal molecules of these substances do not stand in a simple integral proportion to each other. The conclusion is therefore drawn that troilite in reality belongs to the hexagonal system and has been formed in presence of excess of iron, whereas magnetic pyrites has been produced in presence of excess of sulphur.

A. H.

**Metaphosphoric Acids.** By SIMEON M. TANATAR (*Chem. Centr.*, 1898, ii, 257; from *J. Russ. Chem. Soc.*, 1898, 30, 99—103).—The yield of sodium trimetaphosphate obtained by Fleitmann's method of heating sodium ammonium hydrogen phosphate until neutral, is

considerably improved by allowing the molten mass to cool only very slowly. The heat of solution of the trimetaphosphate in water is  $-0.547$  Cal., that of the monometaphosphate in an equivalent quantity of hydrochloric acid or of sulphuric acid is nil, and that of silver metaphosphate,  $\text{AgPO}_3 + \frac{1}{3}\text{H}_2\text{O}$ , is  $-1.683$  Cal. in water and  $+13.893$  Cal. in hydrochloric acid. The heat of neutralisation of trimetaphosphoric acid with sodium hydroxide is  $+15.551$  Cal. *Ethylic trimetaphosphate*, prepared by heating the silver salt with ethylic iodide in absolute alcohol, is insoluble in benzene and cannot be volatilised without decomposition. *Ethylic dimetaphosphate* has a sp. gr.  $1.230$ , is insoluble in benzene, and also decomposes when heated; the sodium and silver salts are not attacked by cold acids.

E. W. W.

**Arsenic Compounds.** By ALFRED PARTHEIL and E. AMORT (*Arch. Pharm.*, 1899, **237**, 121—127).—*Action of arsenic hydride on mercuric chloride.*—The results obtained confirm those of previous observers. When arsenic hydride, largely diluted with hydrogen, is passed into a solution of mercuric chloride in alcohol, the first product is yellow chloromercurarsine,  $\text{AsH}_3 \cdot \text{HgCl}$ . By passing in more arsenic hydride, orange di- and brown tri-chloromercurarsine and black arsenic mercuride,  $\text{AsH}(\text{HgCl})_2$ ,  $\text{As}(\text{HgCl})_3$ , and  $\text{As}_2\text{Hg}_3$ , are obtained in succession. The first two decompose gradually in presence of a solution of mercuric chloride, yielding arsenious acid, hydrochloric acid and mercurous chloride. The third yields mercurous chloride and arsenic under these circumstances; moreover, it is easily decomposed by water, with formation of arsenious acid, hydrochloric acid, and mercury. Arsenic mercuride, when dry, oxidises readily in the air to arsenious oxide and mercury.

C. F. B.

**Decomposition of Carbonic Oxide in Presence of Metallic Oxides.** By O. BOUDOUARD (*Compt. rend.*, 1899, **128**, 822—824).—The decomposition of carbonic oxide at  $650^\circ$  in presence of ferric oxide, nickel oxide, and cobalt oxide is a function of the time, and within certain limits depends on the quantity of metallic oxide present. Whereas at  $445^\circ$  the decomposition is complete (this vol., ii, 287), at  $650^\circ$  it is limited, and in presence of cobalt oxide decomposition ceases when the gaseous mixture contains 61 per cent. of carbonic anhydride and 39 per cent. of carbonic oxide.

C. H. B.

**Decomposition of Carbonic Anhydride in Presence of Carbon.** By O. BOUDOUARD (*Compt. rend.*, 1899, **128**, 824—825).—Carbonic anhydride was heated at  $650^\circ$  with wood charcoal and with carbon obtained by the decomposition of carbonic oxide. In both cases, the proportion of carbonic oxide in the gas gradually increased, the reaction being more rapid with the wood charcoal than with the other. The limit of the reaction with wood charcoal was reached after 12 hours, and the composition of the gaseous mixture— $\text{CO}_2$ , 61 vols.,  $\text{CO}$ , 39 vols.—is identical with the composition of the gas at the limit of the reaction between carbonic oxide and cobalt oxide at the same temperature (preceding abstract).

C. H. B.

**Silicomesoxalic Acid.** By LUDWIG GATTERMANN and E. ELLERY (*Ber.*, 1899, 32, 1114—1116).—Silicon octochloride,  $\text{Si}_2\text{Cl}_8$  (Gattermann and Weinlig, *Abstr.*, 1894, ii, 414), is best obtained by acting with chlorine on silicon in the preparation of which an excess of magnesium has been employed; if the whole of the magnesium silicide has been previously removed by extracting the silicon with hydrochloric acid, little of the octochloride is obtained, so that its formation appears to be due to the presence of the silicide.

When the purified octochloride is left exposed to the air in a platinum dish at  $0^\circ$ , hydrogen chloride is evolved, and *silicomesoxalic acid*,  $\text{Si}(\text{OH})_2(\text{SiOOH})_2$ , obtained as a white powder, which does not dissolve in cold water, but is decomposed by hot, giving rise to hydrogen and silica; the acid, when dry, is extremely unstable, and often decomposes spontaneously, becoming incandescent; it rapidly reduces a warm alkaline solution of potassium permanganate.

W. A. D.

**Silver Suboxide.** By ANTOINE GUNTZ (*Compt. rend.*, 1899, 128, 996—998).—When dry silver oxide is heated at  $358^\circ$  for 40 hours in a closed tube fitted with a manometer, the pressure remains stationary at 49 atmospheres; if this temperature is maintained while some of the oxygen is allowed to escape, the pressure falls and then rises until the maximum is again attained. Two tared open tubes, one containing silver and the other silver oxide, were heated in a sealed tube containing so much potassium permanganate that when the temperature was raised to  $358^\circ$  the pressure of the liberated oxygen exceeded 49 atmospheres. After remaining at this temperature for three days, the tube was rapidly cooled, and the enclosed tubes weighed; the one containing silver had gained 3.88 per cent. in weight, whereas that containing silver oxide had lost 3.39 per cent. The gain in weight calculated on  $4\text{Ag} + \text{O} = \text{Ag}_4\text{O}$  should be 3.67, whilst the loss calculated on  $2\text{Ag}_2\text{O} = \text{Ag}_4\text{O} + \text{O}$  should be 3.44. This experiment indicates that the dissociation pressure of the sub-oxide  $\text{Ag}_4\text{O}$  at  $358^\circ$  is approximately 49 atmospheres.

G. T. M.

**Solubility of Ammonia in Aqueous Solutions of Silver Nitrate.** By DMITRI P. KONOWALOFF (*Chem. Centr.*, 1898, ii, 659; from *J. Russ. Chem. Soc.*, 1898, 30, 367—374).—If in the case of saturated solutions of ammonia in aqueous solutions of silver nitrate, twice the number of molecules of silver nitrate present is subtracted from the number of dissolved molecules of ammonia, the remaining ammonia shows the same solubility as in pure water, and Henry and Dalton's law is applicable. The same formula,  $H = 56.58(m - 2n)$ , applies in both cases, where  $H$  is the vapour tension of the ammonia in millimetres of mercury,  $m$  the number of molecules of ammonia, and  $n$  the number of molecules of silver nitrate in 1 litre. The solubility of ammonia in aqueous solutions of the compound  $\text{AgNO}_3 \cdot 2\text{NH}_3$  is, as in the case of its solution in ammonium or sodium nitrate solutions, the same as in pure water.

E. W. W.

**Preparation and Properties of Crystallised Calcium Phosphide.** By HENRI MOISSAN (*Compt. rend.*, 1899, 128, 787—793).—Calcium phosphide,  $\text{Ca}_3\text{P}_2$ , can be obtained in a crystalline form by

heating an intimate mixture of calcium phosphate, 310 parts, and lamp black, 96 parts, in an electric furnace with a current of 950 ampères and 45 volts, also by heating the amorphous phosphide with a current of 800 ampères and 50 volts. It is red-brown in colour, melts with difficulty except in the electric furnace, and has a sp. gr. 2.51 at 15°. If the action of the electric arc is continued too long, part of the phosphide is decomposed.

When phosphorus vapour is passed over calcium heated to dull redness in a vacuum, calcium phosphide is formed with incandescence, but the product is amorphous. Calcium phosphide is not affected by hydrogen or nitrogen at 900°, but at 1200° is slightly decomposed by the latter and a small quantity of nitride is formed. Boron and carbon are without action at 700°, but at a higher temperature carbon converts it into calcium carbide. Arsenic has no action at the melting point of glass.

Chlorine has no action on the phosphide in the cold, but attacks it readily at about 100°, and bromine and iodine behave in the same way at somewhat higher temperatures. Oxygen and sulphur decompose the phosphide with incandescence at about 300°. Oxidising agents, including nitrous and nitric oxides, attack it very readily at a red heat, and the halogen hydracids decompose it with great energy. Concentrated nitric and sulphuric acids are without action, but in presence of water the phosphide is rapidly decomposed. Water acts somewhat slowly on the crystallised phosphide, and if it has been heated sufficiently in the electric furnace, the liberated hydrogen phosphide is not spontaneously inflammable; the reaction is complex and all the phosphorus is not liberated in the form of hydride. Ordinary organic solvents have no action on the phosphide. C. H. B.

**Reduction of Calcium Phosphate by the Carbon of the Electric Arc.** By ALBERT RENAULT (*Compt. rend.*, 1899, 128, 883—884).—A mixture of carbon and tricalcium phosphate is introduced into an iron or carbon crucible forming the cathode of an electric arc, and the carbon anode is thrust into the crucible until the current passes. When the circuit is made, fumes containing phosphorus are evolved, and resistances are introduced until the evolution of vapour ceases; in one experiment, this result was attained with a current of 20 ampères and an E.M.F. of 22 volts. The product consists of calcium phosphide,  $\text{Ca}_3\text{P}_2$  (compare preceding abstract), which is obtained in reddish granules embedded in a mixture of carbon and unaltered phosphate. The phosphide has a crystalline fracture, but is so readily decomposed by moisture that the surface exposed becomes rapidly coated with white calcium hydroxide. When treated with water, it evolves gaseous hydrogen phosphide, which is entirely absorbed by copper sulphate, and is not spontaneously inflammable. Under certain conditions, a mixture of calcium phosphides is obtained which gives rise to both liquid and gaseous hydrogen phosphides. G. T. M.

**Solubility of Tricalcium Phosphate and Apatite in Water.** By JULES JOFFRE (*Bull. Soc. Chim.*, 1898, [iii], 19, 372—375).—One litre of water was found to dissolve 0.009 gram of tricalcium phosphate and 0.002 gram of apatite, whilst in water saturated with carbonic

anhydride at the ordinary pressure the solubilities were 0.153 and 0.014 gram per litre respectively. These results were obtained by leaving the substances in contact with water for about two months, filtering, and estimating the phosphoric acid in the filtrate as ammonium phosphomolybdate. The author is of opinion that the vegetable acids contained in the roots of plants have no action on phosphates, the solution of the latter being effected mainly through the agency of carbonic anhydride. Superphosphate, when applied to the soil, is by the action of the calcium carbonate present converted gradually into tricalcium phosphate, which is thus disseminated through the soil in a condition favourable to the solvent action of water.

N. L.

**Phosphorescence of Strontium Sulphide.** By JOSÉ R. MOURELO (*Compt. rend.*, 1899, 128, 557—559).—Strontium sulphide shows a more intense and persistent phosphorescence when excited by diffused light than when exposed to direct sunlight. Calcium, barium, and zinc sulphides show the same peculiarity. Exposure to diffused light makes the strontium sulphide more sensitive to subsequent exposures, whereas exposure to direct sunlight reduces the sensitiveness and may destroy it altogether. By repeatedly exposing strontium sulphide for a short time to diffused light, it becomes so sensitive that marked phosphorescence is excited by the light of one candle. The same sulphide shows intense phosphorescence when heated at a temperature considerably below a red heat.

If an unexposed tube of the sensitive sulphide is placed in a box between two tubes of exposed and phosphorescing sulphide, it is found after a time that phosphorescence in the middle tube has been excited by the others. Further, if a considerable mass of the sulphide is exposed under such conditions that only the surface is affected by light, and is then placed in the dark, it is found after a short time that the whole mass is phosphorescent, but shows zones of decreasing intensity; this phenomenon the author calls *auto-excitation*.

C. H. B.

**Occurrence of Barium Compounds in Artesian Well Water.** By JOHN WHITE (*Analyst*, 1899, 24, 67—71).—Samples of water obtained at different times from an artesian well at Ilkeston, Derbyshire, contained soluble barium compounds, the amount, expressed as barium chloride, on two occasions reaching 38.55, and 40.70 parts per 100,000. This abnormal water is believed to have come, not from the bottom of the boring (1801 feet), but to have obtained access by a fracture of the steel lining of the bore-hole.

L. DE K.

**Mixed Halogen Salts of Lead.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1898, [iii], 19, 598—603).—Since Herty and Boggs (*Abstr.*, 1898, ii, 585) were unable to confirm the existence of a definite lead chloriodide of the composition  $PbICl$ , the action of lead chloride on lead iodide has been studied, and it is found that the chloriodide is always produced, although the extent to which it is accompanied by chloride and iodide, and the order in which the compounds crystallise from the solution, depend on the experimental conditions. Against the

view that the substance in question is an isomorphous mixture, it is urged (1) that by the action of nitric peroxide it is converted into the oxychloride,  $\text{Pb}_2\text{OCl}_2$ , and not into a mixture of chloride and oxide; (2) that it is readily attacked by hydrochloric acid, which is not the case with a mixture of chloride and iodide; (3) that it is extremely sensitive to light, unlike lead chloride and iodide; (4) that lead chloride and iodide crystallise in different systems; (5) that analyses of the products obtained by successive crystallisations indicate the existence of the chloriodide, as is shown graphically.

No compound containing both chlorine and bromine could be obtained by the action of hydrochloric acid on lead bromide, or of hydrobromic acid on lead chloride. If, however, 10 c.c. of a 10 per cent. solution of potassium bromide is added to a boiling solution of 5 grams of lead chloride in 240 c.c. of water and the liquid slowly cooled, aggregates of cruciform crystals of the composition  $3\text{PbCl}_2, \text{PbBr}_2$  are obtained. This compound is not affected by light, and is insoluble in acetic acid and in chloroform; it is soluble in water, by which it is more or less decomposed, and is also readily decomposed by hydrochloric, hydrobromic, nitric, and nitrous acids.

A lead bromochloride of the composition  $\text{PbBrCl}$ , which will be subsequently described, has been obtained by an indirect method.

N. L.

**Preparation and Properties of Crystalline Copper Subphosphide.** By GEORGES MARONNEAU (*Compt. rend.*, 1899, 128, 936—939).—A copper phosphide having the formula  $\text{Cu}_2\text{P}$  is produced by heating a mixture of copper phosphate and petroleum carbon in the electric furnace for 3—5 minutes with a current of 900 ampères and an E.M.F. of 45 volts. The product, which consists of crystals of the phosphide embedded in metallic copper, is disintegrated by being placed at the cathode of an electrolytic cell containing a saturated solution of copper sulphate; the crystalline deposit is collected and washed with water, alcohol, or ether, and lixiviated with bromoform to remove particles of graphite. The copper phosphide of commerce, when submitted to this treatment, also gives a crystalline deposit of the phosphide  $\text{Cu}_2\text{P}$ . This substance was first obtained by Schrötter, and it has also been prepared by other investigators (*Abstr.*, 1898, ii 474). Its specific gravity is 6.4. When heated at  $1000^\circ$  in an atmosphere of hydrogen, it loses some of its phosphorus; fluorine attacks it at ordinary temperatures, and iodine only at temperatures somewhat below red heat; when warmed in contact with oxygen or sulphur, it is decomposed, yielding oxides or sulphides. It dissolves in nitric acid, aqua regia, and a mixture of nitric and hydrofluoric acids; the latter acid alone has no action on it, and neither has acetic acid, but it is slowly decomposed by hydrochloric and sulphuric acids. G. T. M.

**Action of Hydrogen Sulphide and Alkali Sulphides on Double Cyanides: Cyanosulphides.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 706—715).—When freshly precipitated silver sulphide is treated with potassium cyanide solution, a colourless solution is obtained which contains silver potassium cyanide, potassium sulphide, and excess of potassium cyanide.



Hydrogen sulphide produces a brown coloration, but no precipitate ; if, however, the liquid is mixed with acetic acid, an abundant precipitate of silver sulphide is formed. Further, if the original solution is boiled, it becomes brown, and on now adding hydrogen sulphide or acetic acid, silver sulphide is precipitated. Similarly, if hydrogen sulphide is added to a solution of silver cyanide in excess of potassium cyanide, it first produces a coloration, and subsequently a precipitate, but the filtrate contains a silver salt and hydrogen cyanide and hydrogen sulphide, both the latter being displaceable by air.

In presence of only a slight excess of potassium cyanide, the action of the hydrogen sulphide is complete ; a considerable excess of the cyanide is necessary to keep the silver in solution. Sodium sulphide behaves in the same way as hydrogen sulphide.

In the solutions there is a complex condition of equilibrium between hydrogen sulphide, hydrogen cyanide, and silver potassium cyanide, dependent on the relative stability of hydrogen silver cyanide and silver potassium cyanide, which is increased by the presence of excess of potassium cyanide, but reduced by an increase in temperature or the addition of acetic acid. The decomposition of silver potassium cyanide by hydrogen sulphide produces no thermal disturbance, and the occurrence of the reaction is determined by the removal of the silver sulphide from the sphere of action. In presence of excess of potassium cyanide, which produces a development of heat over and above that corresponding with the formation of silver potassium cyanide, there is no precipitation. If the pure double cyanide is mixed with a quantity of hydrogen sulphide insufficient for complete precipitation, an intermediate condition is produced, and there is development of heat. The action of potassium cyanide solution on freshly precipitated silver sulphide also causes considerable development of heat. The condition of equilibrium seems to correspond with the proportions  $2\text{AgK}(\text{CN})_2 + \text{K}_2\text{S} + 92\text{KCN}$ , a double cyanide and sulphide being formed with development of heat.

Mercuric potassium cyanide shows no similar phenomena, the precipitation by hydrogen sulphide being complete. With sodium sulphide, the results are different, owing to the exothermic formation of a double sulphide. The mercuric sulphide is completely redissolved by the alkali sulphide, provided that it is present in proportion greater than that required by the formula  $\text{HgS} + 2\text{Na}_2\text{S}$ .

When zinc potassium cyanide is mixed with hydrogen sulphide or sodium sulphide, precipitation is slow, and in presence of an excess of potassium cyanide, not smaller than that required by the expression  $\text{Zn}(\text{CN})_2 + 2\text{KCN} + 6\text{KCN}$ , no precipitation of zinc sulphide takes place at all. Freshly precipitated zinc sulphide is dissolved by potassium cyanide solution but is reprecipitated on boiling. The reaction  $\text{Zn}(\text{CN})_2 + 8\text{KCN}$  develops  $+10.8$  Cal. or about  $+2.2$  Cal. above the quantity representing the formation of the double cyanide. The reaction  $[\text{Zn}(\text{CN})_2 + 2\text{KCN} + 6\text{KCN}]$  diss.  $+ \text{H}_2\text{S}$  diss. develops  $+5.0$  Cal., but there is no precipitation of zinc sulphide even after a long time at the ordinary temperature.  $\text{ZnS} + \text{KCN}$  diss. in excess develops  $+9.3$  Cal. and a similar result is obtained if potassium cyanide solution is first mixed with sodium sulphide and zinc sulphate is then added. In the case of zinc, as in the case of silver, a double cyanide-sulphide is formed.

C. H. B.

**Reactions in Anhydrous Solvents.** By ALEXANDER NAUMANN (*Ber.*, 1899, 32, 999—1004).—From a solution of mercuric chloride in ether, benzonitrile, ethylic acetate, benzene, or acetone, hydrogen sulphide precipitates all the mercury as the compound  $2\text{HgS}, \text{HgCl}_2$ . Dry ammonia precipitates the compound  $\text{HgCl}_2, \text{NH}_3$  from a solution of mercuric chloride in benzonitrile, but  $\text{HgCl}_2, 2\text{NH}_3$  from a solution in ethylic acetate or methylal; stannous chloride gives a precipitate of mercurous chloride from all three solutions. Silver nitrate gives a precipitate of silver chloride when added to mercuric chloride dissolved in benzonitrile.

Hydrogen sulphide precipitates all the copper from a solution of cupric chloride in ethylic acetate as cupric sulphide; ammonia gives a precipitate of the compound  $\text{CuCl}_2, 6\text{NH}_3$ , and hydrogen chloride a precipitate of  $\text{CuCl}_2, 2\text{HCl}$ . Stannous chloride throws down cuprous chloride from a solution of cupric chloride in ethylic acetate, and cuprous chloride separates on cooling from a warm mixture of cupric chloride and stannous chloride in benzonitrile. On mixing cadmium iodide and cupric chloride dissolved in ethylic acetate, cuprous iodide and cadmium chloride are precipitated, whilst iodine remains in solution; all other metallic iodides give a similar reaction when dissolved in acetone.

Cupric chloride precipitates silver chloride from a solution of silver nitrate in benzonitrile; sulphur has no action in the cold, but precipitates silver sulphide on heating. Barium iodide and silver nitrate dissolved in pyridine give a precipitate of barium nitrate, leaving silver iodide in solution. Potassium thiocyanate and silver nitrate dissolved in pyridine give a precipitate of potassium nitrate.

The action of various metals, oxides, hydroxides, and salts on solutions of mercuric chloride, cupric chloride, and silver nitrate is also described.

T. M. L.

**Dissociation of Mercuric Oxide.** By H. PELABON (*Compt. rend.*, 1899, 128, 825—828).—When mercuric oxide is heated in sealed tubes in presence of excess of oxygen, the limiting pressures of the oxygen between 440 and 620° are accurately represented by the equation  $\log p = m/T + n \log T + z$ , where  $T$  is the absolute temperature, the constants have the values  $m = -27569$ ,  $n = -57.58$  and  $z = +203.94711$  and the logs. are common logs. At 440°, the pressure of the oxygen is only a few mm., and at 610° it is 1240 mm.

When the initial system consists of mercuric oxide only, the product of the pressure of the oxygen into the square of the pressure of the mercury vapour is a positive number depending only on the temperature, which is in agreement with Duhem's theory.

C. H. B.

**Mercury Derivatives of Nitrogen Compounds.** By KARL A. HOFMANN and EDUARD C. MARBURG (*Annalen*, 1899, 305, 191—222).—See this vol., i, 486.

**Complex Oxides of the Rare Earth Metals.** By GRÉGOIRE WYROUBOFF and AUGUSTE VERNEUIL (*Compt. rend.*, 1899, 128, 501—503).—It is well-known that cerosoceric oxide, although when

pure insoluble in nitric acid, becomes completely soluble in presence of lanthanum or didymium oxide. The authors find that the cerium oxide,  $\text{Ce}_3\text{O}_4$ , does not dissolve completely unless the proportion of lanthanum and didymium present corresponds with that required for the formula  $\text{Ce}_3\text{O}_4, 3\text{MO}$ , where M is La or Di. A cerium oxide,  $\text{Ce}_3\text{O}_4, 3\text{CeO}$ , is already known, and Brauner has described a sulphate corresponding with  $\text{Ce}_3\text{O}_4, 3\text{LaO}$ . When heated in contact with air, the oxides  $\text{Ce}_3\text{O}_4, 3\text{DiO}$  and  $\text{Ce}_3\text{O}_4, 3\text{LaO}$ , unlike the cerium oxide, do not oxidise, and if they become polymerised the change is not indicated by any difference in their behaviour with acids.

If the proportion of didymium or lanthanum is lower than that required to form the oxide  $\text{Ce}_3\text{O}_4, 3\text{MO}$ , the strongly heated mixture will not dissolve in strong nitric acid, but dissolves in the dilute acid and forms a nitrate,  $(\text{Ce}_3\text{O}_4, \text{MO})_{16}, 4\text{HNO}_3 + 2\text{H}_2\text{O}$ , which is precipitated by nitric acid from its aqueous solution, and has all the properties of the nitrate,  $(\text{Ce}_3\text{O}_4)_{20}, 4\text{HNO}_3 + \text{H}_2\text{O}$ , previously described; it yields an insoluble sulphate, and the oxide is not precipitated until at least half the acid has been saturated by the alkali hydroxide added. The precipitated oxide is white when lanthanum only is present, but deep brown if it contains didymium; it is insoluble in hydrochloric acid, and is attacked with difficulty by a mixture of hydrochloric acid and potassium iodide. When very strongly heated, it becomes  $(\text{Ce}_3\text{O}_4, \text{MO})_n$ , where  $n > 16$ , and is insoluble in all acids except boiling sulphuric acid.

When the monoxides are present in lower proportion than is required to form the oxide  $\text{Ce}_3\text{O}_4, \text{MO}$ , a mixture of the nitrates,  $(\text{Ce}_3\text{O}_4)_{20}, 4\text{HNO}_3 + 2\text{H}_2\text{O}$  and  $(\text{Ce}_3\text{O}_4, \text{MO})_{16}, 4\text{HNO}_3 + 2\text{H}_2\text{O}$ , is obtained and cannot be resolved into its proximate constituents.

The existence of these stable complex oxides explains the rose or salmon colour of imperfectly purified cerium. Praseodymium oxide,  $\text{Pr}_3\text{O}_4$  or  $\text{Pr}_3\text{O}_4, 3\text{PrO}$ , can replace cerium in the molecule  $\text{Ce}_3\text{O}_4, \text{MO}$ .

Oxides of the yttrium group behave in the same way as those of the cerium group, and form corresponding complex oxides and nitrates.

These mixed oxides form polymerides analogous to, but much less stable than, the polymerides of the pure cerium oxides. They are somewhat difficult to prepare, but if a mixture of equal parts of the oxides,  $\text{Ce}_3\text{O}_4, \text{LaO}$  and  $\text{DiO}$ , is very strongly heated and then treated at  $50^\circ$  or  $60^\circ$  with 10 times its weight of dilute nitric acid (1 : 8), the supernatant liquid contains the excess of the monoxides, whilst the precipitated dissolves easily in water, and can be purified by reprecipitation with nitric acid. The nitrate has the composition  $(\text{Ce}_3\text{O}_4, \text{MO})_4, 4\text{HNO}_3 + \text{H}_2\text{O}$ , and is very deep garnet red when the monoxide is didymium oxide. Precipitation of the oxide does not begin until half the acid has been saturated by the alkali; the chloride is insoluble in hydrochloric acid, and the sulphate is insoluble and is decomposed by water and converted into a salt of the type  $(\text{Ce}_3\text{O}_4, \text{MO})_4, \text{H}_2\text{SO}_4$ . C. H. B.

**Nature of the Didymium accompanying Yttrium in Monazite Sands.** By G. URBAIN (*Bull. Soc. Chim.*, 1898, [iii], 19, 381—382).—The didymium oxide which Boudouard separated from

the yttrium metals of monazite sands, although exhibiting all the characteristics of neodymium, is not identical therewith, and contains a considerable proportion of other oxides. The spectrum shows, besides the bands of neodymium, Soret's X-bands and some very feeble bands of erbium and praseodymium. Fractional precipitation with potassium sulphate in alcoholic solution indicates the presence of metals of the terbium group, and fractionation with ammonia in presence of hydrogen peroxide shows the presence of cerium. Of the praseodymium bands observed, 4690 is quite distinct, whilst 4440 and 4820 are faint.

N. L.

**Properties and Applications of Aluminium.** By ALFRED DITTE (*Compt. rend.*, 1899, 128, 793—799).—Alloys of aluminium with 3 per cent. of copper and with 5 to 6 per cent. of copper, together with about 1 per cent. of impurities, consisting chiefly of iron (0.29—0.37), silicon (0.37—0.54), and traces of carbon, behave in much the same way as pure aluminium in contact with dilute acids, saline solutions, &c. (this vol., ii, 292). When heated to dull redness, the surface becomes rough and vesicular, and if the metal is tempered in water, it acquires a confusedly crystalline structure and becomes brittle, the surface being covered with fine cracks.

Dilute sulphuric acid (2:100) dissolves the metal slowly, the surface becoming covered with a black layer of finely divided copper mixed with iron and silicon. The tempered metal behaves similarly, but acquires a somewhat different appearance.

Dilute solutions of alkali carbonates (2:100), sodium chloride solution (8:1000), and sea water, in presence of air, attack the alloys somewhat readily, the surface becoming covered with gelatinous aluminium hydroxide in which opaque, anhydrous aluminium oxide gradually separates (*loc. cit.*). Polished surfaces of the metal quickly lose their brightness and are attacked in a similar way.

Various articles of aluminium used by the French army in Madagascar were examined. Part of a portable cistern showed considerable deterioration: it was coated with aluminium hydroxide and oxide, was more or less disintegrated and brittle, and dissolved somewhat readily in dilute acids. This result was doubtless due to the presence of a small quantity of salt in the water. Smaller articles used for cooking and the like also showed considerable corrosion and disintegration, due to the action of the sodium chloride contained in the food, and of weak acids such as vinegar, or possibly the juices of fruit.

C. H. B.

**Application of Aluminium.** By HENRI MOISSAN (*Compt. rend.*, 1899, 128, 895—901. Compare *Abstr.*, 1894, ii, 450; 1896, ii, 301, 338; 1897, ii, 602; and 1898, ii, 118, 292).—Analyses are given showing the improvement which has been made in the quality of commercial aluminium during the period 1893—1897. The author disagrees with the conclusions drawn by Ditte from his experiments on the action of solutions of various acids, alkalis, and salts on the metal (see preceding abstract). An exhaustive trial of aluminium culinary utensils was made by the French army during the Madagascar campaign, and the satisfactory results obtained are distinctly in favour

of the employment of aluminium for cooking utensils. The metal is easily stamped into vessels of the required shape, and the danger attending the use of soldered utensils is thereby avoided; aluminium vessels, moreover, are very easily cleaned. G. T. M.

**Application of Aluminium.** By ALFRED DITTE (*Compt. rend.*, 1899, 128, 971—975).—In reply to Moissan's observations on the application of aluminium (see preceding abstract), the author points out that the thin layer of grease which is produced on aluminium cooking utensils cannot be removed except by the aid of alkaline solutions, and these have such an erosive action on the metal that the vessels are speedily rendered useless. The lightness of the metal, the ease with which it can be worked, and the innocuous character of its compounds are all points in favour of its application, but its great heat of combustion is a serious drawback. The value of this constant is 131 Cal.; it is twice as great as that of iron (64.4 Cal.), and almost equal to that of calcium (145 Cal.) G. T. M.

**Double Iodates of Manganese [Tetrioate].** By ARMAND BERG (*Compt. rend.*, 1899, 128, 673—676).—Hydrated manganese dioxide dissolves in a concentrated solution of iodic acid, forming a brown liquid from which it is impossible to separate manganic iodate in a solid form. In the presence of certain metallic iodates, double salts are produced of far greater stability.

*Manganic potassium iodate*,  $\text{Mn}(\text{IO}_3)_4 \cdot 2\text{KIO}_3$ , obtained by boiling together iodic acid (3 mols.), hydrated manganese dioxide (1 mol.), and excess of potassium iodate, rapidly separates as an insoluble, brownish-violet, crystalline powder. The crystals are approximately cubic, and have scarcely any action on polarised light.

*Manganic ammonium iodate*,  $\text{Mn}(\text{IO}_3)_4 \cdot 2\text{NH}_4\text{IO}_3$ , resembles the potassium salt, and is prepared in a similar manner.

*Manganic barium iodate*,  $\text{Mn}(\text{IO}_3)_4 \cdot \text{Ba}(\text{IO}_3)_2$ , produced by boiling the hydrated dioxide with the requisite amount of finely-powdered barium iodate and a slight excess of iodic acid, is precipitated as a yellowish-brown, crystalline powder mixed with colourless particles of barium iodate; the latter can be removed by levigation.

*Manganosomanganic iodate*,  $\text{Mn}^{\text{IV}}(\text{IO}_3)_4 \cdot \text{Mn}^{\text{II}}(\text{IO}_3)_2$ , is obtained either in small, bluish-grey needles or in dark violet, radiate clusters; its constitution may be that of a sesqui-salt,  $\text{Mn}_2^{\text{III}}(\text{IO}_3)_6$ . The sodium and calcium double iodates were not produced by the method which yielded the corresponding potassium and barium salts. G. T. M.

**Absorption of Nitric Oxide by Ferrous Salts.** By VICTOR THOMAS (*Bull. Soc. Chim.*, 1898, [iii], 19, 419—422. Compare Abstr., 1897, ii, 145 and 262; also this vol., ii, 368).—The author has repeated and extended the experiments of Gay and Graham on the absorption of nitric oxide by ferrous salts, and confirms the results obtained by those observers. It is found that all ferrous salts, without exception, absorb nitric oxide in aqueous solution, and also when dissolved in alcohol, ether, acetic acid, or ethylenic bromide. The two latter solvents deposit ferrous salts in the anhydrous condition on evaporation, and hence it is inferred that the absorption is due to

the salts themselves and not to their hydrates. The amount of nitric oxide absorbed depends on the nature of the solvent, and is greater for alcoholic than for aqueous solutions. N. L.

**New Method for Preparing Iron Silicide.** By PAUL LEBEAU (*Compt. rend.*, 1899, 128, 933—936).—Iron silicide,  $\text{FeSi}$ , is conveniently prepared by heating a mixture of 10 parts of commercial copper silicide and 1 part of iron filings for 5 minutes in the electric furnace, a current of 950 ampères being employed with an E.M.F. of 45 volts; the cooled product exhibits a homogeneous fracture like that of copper silicide. It is broken up and treated with 50 per cent. nitric acid to decompose copper silicide, and when the whole mass is disintegrated, it is washed repeatedly with water and then heated with dilute caustic soda. The tetrahedric crystals of iron silicide thus obtained have a brilliant metallic lustre; they can be freed from the last traces of copper silicide by repeating the above treatment. The specific gravity of the crystals is 6.17 at  $15^\circ$ , and in hardness they are intermediate between quartz and corundum. The substance is not affected by oxygen or hydrogen at a red heat; fluorine attacks it at the ordinary temperature, forming iron fluoride, the substance becoming incandescent; chlorine and bromine produce a similar effect at a low red heat. The silicide is not attacked by mineral acids employed singly, but a mixture of nitric and hydrofluoric acids dissolves it completely; it is readily attacked by molten alkalis or mixtures of alkali nitrates and carbonates.

By the direct union of iron and silicon at the temperature of the electric furnace, Moissan obtained the lower silicide,  $\text{Fe}_2\text{Si}$  (Abstr., 1896, ii, 173), and by the direct action of carbon on tungsten the carbide  $\text{CW}_2$  was produced. Williams (Abstr., 1898, ii, 594), by reducing tungstic acid with carbon in the presence of iron carbide, obtained the higher carbide CW. These results indicate that the presence of a metallic compound serving as a solvent gives rise to combinations of a different order from those which occur between the elements themselves, the chemical action being moderated by dilution with the solvent, so that the combination takes place at lower temperatures; both the silicide  $\text{FeSi}$  and the carbide CW are decomposed when heated alone at higher temperatures. Copper silicide at high temperatures readily gives up its silicon to cobalt, nickel, and chromium, and similar effects are observed in the case of the arsenide and antimonide of this metal. G. T. M.

NOTE.—For the action of zinc on copper silicide, see Abstr., 1898, ii, 474.

**Hydrates of Cobalt Iodide and Ferric Bromide.** By I. BOLSCHAKOFF (*Chem. Centr.*, 1898, ii, 660; from *J. Russ. Chem. Soc.*, 1898, 30, 386—391).—By the action of iodine on cobalt under water, a red solution is formed from which the hydrate  $\text{CoI}_2 + 6\text{H}_2\text{O}$  separates on slightly evaporating and then strongly cooling, whilst the mother liquor, on cooling, yields the hydrate  $\text{CoI}_2 + 9\text{H}_2\text{O}$ . The latter crystallises in thin, red, rhombic plates, is very hygroscopic, and loses  $3\text{H}_2\text{O}$  at  $6.4^\circ$ .

The hydrate of ferric bromide,  $\text{FeBr}_3 + 6\text{H}_2\text{O}$ , separates in spherical clusters of small, dark green needles when the dark brown solution prepared by the action of bromine on iron under water is slightly evaporated and then placed in a desiccator over sulphuric acid; it is soluble in alcohol and ether, and melts at  $27^\circ$  without decomposing.

E. W. W.

**Tungsten Bisulphide.** By ED. DEFACQZ (*Compt. rend.*, 1899, 128, 609—611. Compare Abstr., 1896, 912; 1898, ii, 521, and this vol., ii, 159).—Tungsten bisulphide is prepared, either by passing hydrogen sulphide over tungsten hexachloride heated at  $375\text{--}550^\circ$  or by fusing a mixture of potassium carbonate, flowers of sulphur, and tungsten trioxide. It is obtained by the former method in black, amorphous scales and by the latter in friable crystals with a blue reflex; it has a sp. gr. 7.5 at  $10^\circ$ . The substance is stable at red heat, but when heated in the electric furnace it gradually loses sulphur. It is reduced by hydrogen at  $800^\circ$ ; fluorine attacks it at ordinary temperatures, chlorine at  $400^\circ$ , giving rise to the hexachloride, whilst the reaction with bromine is incomplete at  $700^\circ$ . Mineral acids, employed singly, are without action on the substance; it is, however, attacked by mixtures of nitric acid with hydrofluoric or hydrochloric acid. Molten alkalis and alkali carbonates dissolve it readily, and the method employed in its analysis is based on the solvent action of a fused mixture of potassium nitrate and carbonate.

G. T. M.

**Bismuth Suboxide.** By LUDWIG VANINO and F. TREUBERT (*Ber.*, 1899, 32, 1072—1081).—As a consequence of Schneider's criticism (this vol., ii, 227), the authors have repeated and extended their experiments, and adhere to their former conclusion, that "the supposed bismuth suboxide is not to be regarded as a homogeneous substance, but as a mixture of bismuth and bismuth oxide." It is a mistake to suppose that they always used the stannous solution in excess. In all cases the precipitate obtained is a mixture of bismuth and bismuth oxide, which can be separated with glycerol and caustic soda, or with tartaric acid and caustic alkali, as well as with hydrochloric acid; the amount of metallic bismuth is always equivalent to the amount of stannous compound employed.

Schneider's chestnut brown solution of a supposed bismuthostannate, obtained by mixing bismuth tartrate with stannous chloride in neutral or feebly alkaline solution, probably owes its colour to the presence of colloidal bismuth in solution; the bulk of the stannous chloride is still present as such. When more alkali is added, less stannous salt, but more metallic bismuth, can be found in the solution.

The properties ascribed by Schneider to his supposed bismuth subsulphide,  $\text{BiS}$ , are found to be equally characteristic of an intimate mixture of finely divided bismuth and bismuth sulphide.

C. F. B.

**Properties and Preparation of Bismuth Tetroxide and Bismuthic Acid.** By CHRISTIAN DEICHLER (*Zeit. anorg. Chem.*, 1899, 20, 81—120).—A critical account of the earlier work on the oxides

of bismuth is given, the present research being undertaken in order to clear up the discrepancies which occur in the results of previous authors. A large number of experiments on the preparation of bismuth tetroxide and bismuthic acid by the action of chlorine on bismuth trioxide suspended in a solution of potassium hydroxide gave the following results: With potassium hydroxide of sp. gr. 1.05—1.5 at 15°, the bismuth trioxide is unaltered. With potassium hydroxide of sp. gr. 1.05—1.35 at 95—100° in the ratio  $\text{KOH}:\text{Bi}_2\text{O}_3=10-20:1$ , a mixture of tetroxide and trioxide is obtained which yields the tetroxide when treated with hot dilute nitric acid; the yield of tetroxide increases with the proportion and concentration of the potassium hydroxide. With potassium hydroxide of sp. gr. 1.35—1.38 at 100—110°, a mixture of potassium bismuthate, tetroxide, and trioxide is obtained which, when treated with hot dilute nitric acid, yields a mixture of the tetroxide and its hydrate,  $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , and with hot concentrated nitric acid forms a small quantity of this hydrate. With potassium hydroxide of sp. gr. 1.39—1.5 at 110—120° in the proportion  $\text{KOH}:\text{Bi}_2\text{O}_3=20-30:1$ , a mixture of potassium bismuthate with lower oxides is obtained which, when treated with hot dilute nitric acid, yields a mixture of tetroxide, bismuthic acid, and potassium bismuthate and with hot concentrated nitric acid, if expeditiously treated, yields bismuthic acid, or when left in contact with it, the hydrated tetroxide; the yield of potassium bismuthate increases with the proportion and the concentration of the potassium hydroxide. With potassium hydroxide of sp. gr. 1.52—1.62 at 120—125° in the proportion  $\text{KOH}:\text{Bi}_2\text{O}_3=10-30:1$ , a mixture of potassium bismuthate with lower oxides containing alkali is obtained which, when treated with hot concentrated nitric acid, yields a mixture of bismuthic acid and hydrated tetroxide, the yield of bismuthic acid decreasing with the concentration of the potassium hydroxide.

Potassium bismuthate is easily prepared by the action of nascent chlorine on bismuth trioxide suspended in potassium hydroxide. Bismuth trioxide (10 grams) is mixed with potassium hydroxide (150 grams, sp. gr. = 1.42—1.45) and potassium chloride (15 grams) and the solution electrolysed in a platinum dish, using the dish as anode and a platinum plate as cathode, the latter being protected by a porous diaphragm in order to prevent the deposition of bismuth. A current density of 2—3 ampères per centimetre is employed, and the temperature is kept just below that of the boiling point of the solution. The bismuthate is deposited as a dense red precipitate which adheres firmly to the dish and is easily washed with water, the excess of bismuth trioxide remaining in suspension. When the potassium bismuthate is treated for a short time with hot concentrated nitric acid and then washed with water, a mixture of bismuthic acid and the hydrate  $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is obtained containing 95 per cent. of bismuthic acid. The author was unable to obtain the acid in a purer state. If dilute nitric acid is employed, a large quantity of  $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  is formed and by the prolonged action of nitric acid of sp. gr. 1.3, the tetroxide dihydrate,  $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , is obtained as an orange-yellow powder. The same compound is also obtained by the action of warm acetic acid on bismuthic acid. Potassium bismuthate, when heated at



120°, loses a small quantity of water and turns black; at 300°, two atomic proportions of oxygen are evolved and  $\text{Bi}_2\text{O}_3 \cdot \text{K}_2\text{O}$ , a yellowish-white substance, is obtained; this is extremely hygroscopic and absorbs water from the air with development of heat, and is decomposed into potassium hydroxide and bismuthic acid. Bismuthic acid, when heated at 100—120°, loses water and turns brown and then black with evolution of oxygen; at 300°, it suddenly turns bright red, and acquires the ordinary yellow colour of the trioxide at 400—500°. The bright red compound obtained at 300° is an allotropic modification of the trioxide; on cooling, it becomes golden yellow; when exposed to sunlight for a few days, it is converted into ordinary trioxide and does not turn red again on heating at 300°; if, however, it is kept in the dark in a closed vessel, it does not alter during two months and then gradually changes into the ordinary modification.

An examination of the electrolysed solution obtained in the preparation of potassium bismuthate shows that the trioxide and bismuthate are slightly soluble in strong potassium hydroxide solution and are obtained as a voluminous precipitate on dilution with water. Bismuthic acid is also slightly soluble, and is precipitated on dilution as bismuth tetroxide dihydrate. In the preparation of potassium bismuthate, the concentration of the potassium hydroxide must not fall below sp. gr. 1.4, as with a solution of sp. gr. 1.37, only a small quantity of bismuthate is deposited, and the suspended bismuth trioxide turns brown and is converted into the tetroxide.

Sodium bismuthate cannot be prepared by this method; no deposit of salt is obtained and the suspended bismuth trioxide turns brown; when the product is poured into water, a bright yellow precipitate is obtained which seems to be a mixture of sodium bismuthate and the trioxide.

When a solution of bismuth trioxide in an alkaline tartrate is oxidised by the electric current (1 ampère per centimetre), a small quantity of the anhydrous tetroxide is obtained, but with a higher current density, the trioxide is deposited. A small quantity of the tetroxide is also obtained by electrolysis in a nitric acid solution.

Bismuth trioxide is not altered when treated with barium peroxide either by fusion or by boiling in the presence of alkali, but is easily converted into the tetroxide by suspending it in potassium hydroxide solution and warming with an excess of potassium persulphate; the product is washed with water and then treated with warm dilute nitric acid or cold acetic acid.

E. C. R.

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### Mineralogical Chemistry.

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**Humic Lignite and Humin.** By C. EG. BERTRAND (*Compt. rend.*, 1898, 127, 823—825).—Generalisations as to the formation of certain lignites deduced from the microscopic study of specimens (compare this vol., ii, 161).

**Plagionite, Heteromorphite and Semseyite.** By LEONARD J. SPENCER, with analyses by GEORGE T. PRIOR (*Min. Mag.*, 1899, 12, 55—68).—The three minerals plagionite, heteromorphite and semseyite are very similar in appearance and physical characters, and the monoclinic crystals are the same in habit, striations, and the pyramidal cleavage (111); they differ in the specific gravity, percentage chemical composition, and in the length of the vertical crystallographic axis *c*.

	<i>a</i>	<i>b</i> : <i>c</i>	$\beta$ .	Formula.	Sp. gr.
Plagionite .....	1.1361	1:0.8410	72° 28'	5PbS, 4Sb <sub>2</sub> S <sub>3</sub>	5.5
Heteromorphite. ....				7PbS, 4Sb <sub>2</sub> S <sub>3</sub>	5.7
Semseyite .....	1.1442	1:1.1051	71° 4'	9PbS, 4Sb <sub>2</sub> S <sub>3</sub>	5.9

In the present paper, three specimens of these plagionite-like minerals are described in detail.

Plagionite from Wolfsberg in the Harz, gave the results under I, agreeing with those required for the formula 9PbS, 7Sb<sub>2</sub>S<sub>3</sub>, which lies between the two formulæ previously given for plagionite, namely, 4PbS, 3Sb<sub>2</sub>S<sub>3</sub> and 5PbS, 4Sb<sub>2</sub>S<sub>3</sub>. The sp. gr. of the group of crystals is 5.57, and of the crystals analysed 5.50.

Heteromorphite occurs at Arnsberg, in Westphalia, as small, indistinct crystals, associated with blende, lining cavities in the massive crystalline material. Analysis II agrees with 11PbS, 6Sb<sub>2</sub>S<sub>3</sub>, which is not far from Pisani's formula 7PbS, 4Sb<sub>2</sub>S<sub>3</sub>. The name heteromorphite is usually placed under jamesonite, but, with Pisani (*Abstr.*, 1877, i, 56), it is here considered to be a distinct species.

Semseyite from Wolfsberg, Harz, gave anal. III, pointing to the formula 21PbS, 10Sb<sub>2</sub>S<sub>3</sub>. The large crystals had been considered to be plagionite, but this analysis proves them to be identical with the semseyite from Hungary (*Abstr.*, 1886, 313).

	Pb.	Sb.	S.	Cu.	Zn.	Total.	Sp. gr.
I.	41.24	37.35	21.10	—	—	99.69	5.50
II.	48.89	31.08	19.36	0.10	0.18	99.61	5.73
III.	51.84	28.62	19.42	—	—	99.88	5.92

All the previous analyses of plagionite-like minerals are quoted and arranged according to the percentage of lead, which varies from 39.36 to 53.16 per cent.; they then fall into three well-marked groups corresponding with the minerals in question. This variation in composition is not to be explained by the intergrowth of galena, or by isomorphous mixing, but it is more probable that the three minerals form a morphotropic series (*Abstr.*, 1894, ii, 241; 1898, ii, 120), in which the vertical crystallographic axis increases in length with an increase in the amount of lead. The slight deviations from the three formulæ, 5PbS, 4Sb<sub>2</sub>S<sub>3</sub>, 7PbS, 4Sb<sub>2</sub>S<sub>3</sub>, and 9PbS, 4Sb<sub>2</sub>S<sub>3</sub> are explained by the more or less parallel intergrowth of the three minerals, giving compound, curved crystals, which in these plagionite-like minerals are very common, so much so that the measurements here given are not sufficient to distinguish between them.

L. J. S.

**Blende and Zinciferous Galena.** By HENRY A. MIERS, with analyses by E. G. J. HARTLEY (*Min. Mag.*, 1899, 12, 111—117).—Blende with metallic lustre.—Bright tetrahedra, black in colour and

with metallic lustre, gave analytical results (I) agreeing with those required for the formula  $5\text{ZnS}, \text{FeS}$ . Very thin fragments are brown by transmitted light. The lustre is so unlike that of ordinary blende that the question arises whether the union of  $\text{ZnS}$  and  $\text{FeS}$  in molecular proportion has not given rise to a mineral having properties distinct from those of a mere isomorphous mixture of the two sulphides.

	Zn.	Fe.	Pb.	Cu.	Mn.	S.	Total.	Sp. gr.
I.	56·83	9·29	—	0·07	trace	33·42	99·61	3·8
II.	4·97	0·67	78·47	—	—	15·07	99·18	

**Zinciferous galena.**—A specimen labelled Bingham, Salt Lake, Utah, consists of brilliant cubes of galena on quartz with pyrites. The small octahedral planes exhibit a marked laminar structure. No traces of blende are seen when the crystals are finely crushed. Analysis II gives the formula  $4\text{PbS}, (\text{Zn}, \text{Fe})\text{S}$ . Previous examples of zinciferous galena have not been obtained in such distinct crystals, and may have been mixtures of galena and blende.

The paper also describes a tetartohedral (?) crystal of pyrites, and the minute cubic crystals of lead produced when a button of the cast metal is etched.

L. J. S.

**So-called "Favas" of Brazilian Diamond-sands.** By EUGEN HUSSAK (*Tsch. Min. Mitth.*, 1899, 18, 334—341).—The name "fava" (bean, pea) is given to small, rounded or flattened pebbles of various colours, compact in structure, and with high specific gravity, which are found in the diamond washings of Brazil. Titanium oxide favas and zirconium oxide favas are described. The former of a blue-grey colour gave analysis I (by W. Florence); thin sections show a homogeneous microcrystalline aggregate of blue-grey grains resembling anatase in appearance. Yellow material gave analysis II; under the microscope, this suggests rutile. The blue-grey titanium oxide favas are the alteration product of perovskite; whilst the yellow-brown favas are paramorphs of rutile after anatase or brookite, or they are pseudomorphs of rutile and anatase after ilmenite. These minerals have been described by Damour and Gorceix as hydrated titanium oxide, but in no case do they contain more than 1 per cent. of water.

	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{V}_2\text{O}_5$ .	Loss on ignition.	Total.	Sp. gr.
I.	98·98	0·15	0·10	0·15	—	0·77	100·15	3·794
II.	98·86	—	—	—	0·86	0·53	100·25	3·8—3·95

The zirconium oxide favas contain over 97 per cent. of  $\text{ZrO}_2$ , and are, therefore, baddeleyite. Those coloured grey and with an earthy fracture have a sp. gr. 4·57—5·01, and contain 2·75 per cent. of water; others are brown to greenish-black and more compact, these have a sp. gr. 5·408, and contain less water (0·5 per cent.). The structure is microcrystalline, and thin sections show the original mineral to have been zircon.

L. J. S.

**Lead Minerals from Laurion: Paralaurionite.** By G. F. HERBERT SMITH, with analysis by GEORGE T. PRIOR (*Min. Mag.*, 1899, 12, 102—110).—Crystallographic and optical determinations are given of

minerals from the ancient lead slags of Laurion in Greece. For laurionite,  $[a:b:c=0.7385:1:0.8346]$ ; several new forms are noted; the refractive indices for sodium light are,  $\alpha=2.0767$ ,  $\beta=2.1161$ ,  $\gamma=2.1580$ . The refractive indices for phosgenite are,  $\omega=2.1181$ ,  $\epsilon=2.1446$  (Na). Fiedlerite has  $[a:b:c=0.8299:1:0.7253]$ ;  $\beta=77^\circ 31'$ , and refractive indices  $\alpha=1.816$ ,  $\beta=2.1023$ ,  $\gamma=2.026$  (Na).

The new mineral, *paralaurionite*, may at a cursory glance be easily mistaken for laurionite or fiedlerite, according as the crystals are prismatic or tabular in habit. It is monoclinic, but almost always pseudorhombic, owing to twinning on  $a(100)$  [ $a:b:c=0.8811:1:0.6752$ ;  $\beta=62^\circ 47'$ ]. Cleavage  $c(001)$ . The optic figure seen through  $a(100)$  is complex owing to the overlapping of two plates in twin position; in this respect, paralaurionite is easily distinguished from the dimorphous mineral laurionite which shows no figure, and from fiedlerite, in which the figure is not central. Index of refraction, 2.1463 (Na). Analysis agrees with the laurionite formula,  $\text{PbClOH}$ .

Pb.	Cl.	H <sub>2</sub> O.	O.	Total.	Sp. gr.
78.1	14.9	3.4	[3.6]	100.0	6.05

The water is eliminated at about  $180^\circ$ , whilst for laurionite it is given off at  $142^\circ$ .

L. J. S.

**Belgian Minerals.** By GIUSEPPE CESÀRO (*Zeit. Kryst. Min.*, 1899, 31, 89—96; from *Mém. Acad. Sci. Belg.*, 1897, 53, 134 pp.).—A detailed description is given of the mineral phosphates, sulphates and carbonates found in Belgium; of the 29 species described, analyses are given of the following:

Phosphorochalcite (pseudomalachite), radially fibrous, with cuprouranite and libethenite in quartz from Viel-Salm; 22.99  $\text{P}_2\text{O}_5$ , 63.88  $\text{CuO}$ , also some  $\text{Al}_2\text{O}_3$ .

Hydrozincite from Bleyberg, dried over sulphuric acid, gave the formula  $3\text{ZnCO}_3, 4\text{Zn}(\text{OH})_2 + 0.4\text{H}_2\text{O}$ , as shown by the following results.

ZnO.	Fe <sub>2</sub> O <sub>3</sub> .	PbO.	PbCl <sub>2</sub> .	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
72.41	0.42	0.36	0.51	16.90	11.31	101.91

L. J. S.

**Chalcophyllite.** By E. G. J. HARTLEY (*Min. Mag.*, 1899, 12, 120—122).—In previous analyses of this mineral, the water has been determined only as loss on ignition, but owing to the presence of arsenic this is not satisfactory. In the present analysis, the water was weighed directly, and sulphuric acid has been found in the mineral for the first time. The material analysed consisted of clear, pale emerald-green crystals, probably from Cornwall. At  $100^\circ$ , there is a loss of 17.93 per cent. of water. When the mineral is heated, there is no change in the optical properties until the crystals suddenly become opaque and cracked.

CuO.	Al <sub>2</sub> O <sub>3</sub> .	As <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	H <sub>2</sub> O.	Total.
45.93	4.74	14.46	7.04	28.26	100.43.

These numbers do not indicate any simple formula.

L. J. S.

**Minerals from Swaziland:** “*Æschynite*” from Hitterö. By GEORGE T. PRIOR (*Min. Mag.*, 1899, 12, 96—101).—A collection of

minerals from the stanniferous gravels of the Embabaan district in Swaziland, South Africa, is described ; it includes cassiterite, monazite, scheelite, corundum, magnetite, garnet, and minerals chemically allied to euxenite and fergusonite.

The "mineral chemically allied to euxenite" occurs as worn, tabular crystals, which in habit and angles are very similar to the large crystals from Hitterö, Norway, described by Brögger under the name of æschynite. It is brownish-black with brilliant vitreous to greasy lustre on the subconchoidal fracture, and has a sp. gr. 4.996. Thin splinters are translucent, yellowish-brown, and isotropic. The results of two analyses are as follows :

Nb <sub>2</sub> O <sub>5</sub> .	TiO <sub>2</sub> .	SiO <sub>2</sub> .	ThO <sub>2</sub> .	SnO <sub>2</sub> .	(Y,Er) <sub>2</sub> O <sub>3</sub> (mol. wt. 246).	(Ce,La,Di) <sub>2</sub> O <sub>3</sub> (mol. wt. 310).	
36.68	21.89	2.12	0.61	0.29	17.11	4.32	
UO <sub>3</sub> .	UO <sub>2</sub> .	FeO.	CaO.	MnO.	MgO.	H <sub>2</sub> O.	Total.
2.14	0.49	5.63	4.12	0.19	0.22	3.69	99.50

The lanthanum and didymium oxides are present in about double the amount of the cerium oxides. Full details of the methods of analysis are given. In chemical composition, the mineral is more closely related to euxenite than to æschynite; the formula suggested is  $2R_2O_3 \cdot 4RO \cdot 6TiO_2 \cdot 4Nb_2O_5 \cdot 5H_2O$ , or  $R_2'''(TiO_3)_3 \cdot 2R'''(NbO_3)_3 + 3R'(TiO_3)_3 \cdot R'(NbO_3)_2 + 5H_2O$ .

In connection with this, crystals from Hitterö agreeing with Brögger's description of "æschynite" were examined qualitatively and found to contain niobic and titanitic acids, yttrium and cerium earths (the latter in much smaller amount than the former), with iron, uranium and calcium, and little or no zirconium or thorium. This result, which agrees with unpublished work by Brögger and Blomstrand, shows that the mineral from Hitterö, analysed by Jehn (1871) and termed by him euxenite, was identical with the crystallised material measured by Brögger: the mineral in question should therefore receive a new name.

Fergusonite (?), in small pebbles or rounded fragments intimately intergrown with monazite, was found to contain water, much niobic acid, iron, uranium, and yttrium earths, but very little titanitic acid or cerium earths. Sp. gr. 5.43, 5.42.

Cassiterite crystals embedded in a quartz felspathic rock are remarkable in being elongated in the direction of the pyramid edge  $[111, \bar{1}\bar{1}1]$ ; this orthorhombic habit is like that recently described for mosseite and tapiolite (Abstr., 1898, ii, 387, 608).

Monazite in rough tabular crystals contains phosphoric acid and cerium earths with some silica and thoria. Sp. gr. 4.62. L. J. S.

**Carnotite, a New Uranium Mineral.** By CHARLES FRIEDEL and E. CUMENGE (*Compt. rend.*, 1899, 128, 532—534).—A new mineral containing uranium and vanadium, to which the authors give the name *carnotite*, is found in yellow, friable masses, mixed with very variable quantities of silica, together with malachite and chessylite, in pockets at the surface of a grit in Montrose Co., Colorado. It is microcrystalline and optically active, but no definite forms could be recognised. The composition of carnotite is represented by the

formula  $2\text{U}_2\text{O}_3, \text{V}_2\text{O}_5, \text{K}_2\text{O} + 3\text{H}_2\text{O}$ ; it contains  $\text{U}_2\text{O}_3$ , 62.46—64.70;  $\text{V}_2\text{O}_5$ , 19.95—20.31;  $\text{K}_2\text{O}$ , 10.97—11.15;  $\text{Fe}_2\text{O}_3$ , 0.65—0.96;  $\text{H}_2\text{O}$ , 5.19, together with traces of copper, lead, and barium, and of the metals described by M. and M<sup>de</sup>. Curie, that give photographically activeradiations. The relative radiating powers, as determined by M. and M<sup>de</sup>. Curie are native mineral, 1.25; mineral free from silica, 2.6; insoluble sulphates (barium and radium), 35; crude sulphides, 11; bismuth and polonium sulphides, 50 to 60.

C. H. B.

**Hardystonite, a New Calcium-zinc Silicate.** By JOHN E. WOLFF (*Proc. Amer. Acad. Arts and Sci.*, 1899, 34, 379—381).—A banded ore specimen from North Mine Hill at Franklin Furnace, New Jersey, consists of grains of willemite, rhodanite, franklinite, and the new mineral hardystonite, named after the Hardystone township in which the Franklin mines are situated. The last mineral is white to transparent with a vitreous lustre. H, 3—4; sp. gr., 3.397—3.395. It fuses with difficulty to a cloudy glass, and is easily gelatinised by hydrochloric acid. Microscopic examination of thin sections shows the mineral to be uniaxial and negative, with a good basal cleavage, and two sets of rectangular prism cleavages at  $45^\circ$  to one another; it is therefore tetragonal. Analysis of material containing a few specks of franklinite and willemite gave,

$\text{SiO}_2$ .	$\text{ZnO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Fe}_2\text{O}_3$ .	Loss on ignition.	Total.
38.10	24.30	1.50	33.85	1.62	0.57	0.52	100.46

Taking the manganese with the zinc, and the magnesium with the calcium, this gives the formula  $\text{ZnO}, 2\text{CaO}, 2\text{SiO}_2$ .

L. J. S.

**Hydrated Aluminium Silicates.** By S. KASAI (*Zeit. Kryst. Min.*, 1899, 30, 653; from *Inaug.-Diss. München*, 1896, 35 pp.).—Experiments have been made in order to test Groth's view (*Tabell. Uebers. d. Min.*) that the amorphous aluminium silicates, for example, allophane, are intimate mixtures of colloidal silica and colloidal alumina. Solutions of colloidal silica and alumina, when brought together, give an amorphous precipitate containing variable amounts of silica, alumina and water. Complete precipitation occurs only when the proportion is  $3\text{SiO}_2 : \text{Al}_2\text{O}_3$ ; with other proportions, the excess partly remains in solution and is partly precipitated. These amorphous precipitates, in their variable composition and instability in the presence of acids, agree completely with the natural substances.

Kaolin has been considered by Schloesing to exist in the colloidal as well as in the crystalline state, and to the minute globules of colloidal kaolin he attributed the plasticity of clay. The apparently amorphous globules in kaolin from Zettlitz, Bohemia, however, are seen under a high magnification to consist of feebly birefringent plates. Further, the plasticity of clay is only dependent on the degree of subdivision of the particles of crystallised kaolin. From the Zettlitz kaolin, dilute sulphuric acid extracts alumina, but very little silica, and analysis of the material after it has been treated with acid only gives the normal kaolin formula. In this case, the excess of alumina must be present as crystallised diaspor, bauxite, or gibbsite, these being very similar to kaolin in optical characters, and they may also, with kaolin, be derived from felspar.

L. J. S.

**A New Variety of Hornblende.** By REGINALD A. DALY (*Proc. Amer. Acad. Arts and Sci.*, 1899, 34, 433—437).—Goniometric measurements and optical determinations are given of crystals of hornblende from Philipstad, Sweden. The angle of optical extinction on the plane of symmetry is  $\epsilon$ :  $\epsilon' = 15^\circ 9'$ ,  $2V = 50^\circ$  about. Absorption,  $\alpha$  = light brownish-green,  $\beta$  = dark yellow-green,  $\gamma$  = dark blue-green;  $\beta > \epsilon > \alpha$ . Sp. gr. 3.275; for the inner, darker zone, 3.230, and for the outer, lighter zone, 3.195. An analysis by Pisani gave

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss on ignition.	Total.
45.20	0.84	7.34	7.55	15.80	1.52	12.30	8.40	0.80	0.37	0.70	100.82

This composition cannot be expressed by any definite formula. The reasons for considering this hornblende distinctive enough to receive the new name *philipstadite* are summarised as follows: "This hornblende is thus unique among the species yet described in that it possesses the combination of properties including an unusually small optic angle, an unusual pleochroism and absorption scheme, a well developed zonal structure, and quite anomalous etch-figures with hydrofluoric acid on the prism (110) and on the clinopinacoid." L. J. S.

**Rocks from Antarctic Regions.** By GEORGE T. PRIOR (*Min. Mag.*, 1899, 12, 69—91).—Petrographical notes are given of the rock-specimens collected in Antarctic regions during the voyage of H.M.S. *Erebus* and *Terror*, under Sir James Clark Ross, in 1839—1843. The collection includes, for the most part, basalts, together with palagonite-tuff, phonolite, rhyolite, dolerite, epidiorite, granite, chert, calcareous glauconitic sandstone, quartz-grit, slate and gneiss; some of these are only represented by pebbles taken from the stomachs of seals and penguins. Analyses are given of the following:—

Silicified globigerinal limestone from Campbell Island (lat.  $52^\circ 33'$  S., long.  $169^\circ 8'$  E.) gave:

SiO <sub>2</sub> .	CaCO <sub>3</sub> .	MgCO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> (Fe <sub>2</sub> O <sub>3</sub> ).	H <sub>2</sub> O, &c.	Total.	Sp. gr.
57.46	39.26	0.36	1.48	[1.44]	100.00	2.15

Basalt (nepheline-basanite?) from Franklin Island (lat.  $76^\circ 8'$  S., long.  $168^\circ 12'$  E.), is a black, compact rock, with olivine, magnetite, augite, feldspar and possibly nepheline; analysis I contains also a trace of tin.

Basalt from Cockburn Island (lat.  $64^\circ 12'$  S., long.  $56^\circ 49'$  W.) gave II; the material analysed was taken from a large specimen at seven inches from the outer zone of basalt-glass; analysis of the glass gave III. Towards the surface of the specimen, the glass increases, and the magnetite decreases, in amount.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss on ignition.	Total.	Sp. gr.
I. 45.61	3.48	15.70	6.17	7.29	trace	6.34	4.84	2.67	5.06	2.34	2.87	99.50	2.87
II. 48.97	1.62	16.12	1.90	9.63	trace	8.73	7.64	1.21	2.99	1.39	100.20	2.89	
III. 50.22	1.95	16.20	3.13	8.07	trace	8.57	7.54	1.38	3.36	0.22	100.64	2.79	

L. J. S.

**A Tachylite from the Bottom of the North Atlantic.** By PIERRE TERMIER (*Compt. rend.*, 1899, 128, 849—851).—A specimen of rock dredged from the bottom of the Atlantic at a depth of 3100 metres, in latitude  $47^\circ 0'$  N. and longitude  $29^\circ 40'$  W. of Paris, was found to have all the microscopic and general characters of a tachylite or basaltic glass. Its high sp. gr., 2.784 at  $20^\circ$ , and the presence of a large proportion of olivine, indicate that it must have a highly basic



character. It is noteworthy that this specimen was dredged from a part of the Atlantic where the bottom is known to be formed by the highest submarine mountain summits. C. H. B.

**Chemical Changes in Oceanic Deposits.** By W. NOEL HARTLEY (*Proc. Roy. Soc. Edin.*, 1897, 21, 25—34).—The views of Murray and Irvine (*Trans. Roy. Soc. Edin.*, 37, pt. 2, No. 23, and *Nature*, 1895, 51, 304) are criticised, and the following conclusions given: (1) The sulphates in fresh- and sea-water mud are reduced to carbonates and hydrogen sulphide by the fermentation of cellulose through the agency of bacteria. (2) There is no evidence of the formation of calcium sulphide or of calcium hydrosulphide. (3) Hydrogen sulphide is not oxidised simply by atmospheric air to sulphuric acid at the ordinary temperature. (4) Sulphur bacteria separate sulphur from hydrogen sulphide, and then oxidise it to sulphuric acid, which acts on the carbonates and again forms sulphates. (5) The formation of manganese carbonate appears to be due to an action on manganic oxide similar to that which operates on sulphates in the presence of fermenting cellulose.

JOHN MURRAY and ROBERT IRVINE reply to these criticisms in a later paper (*Proc. Roy. Soc. Edin.*, 1897, 21, 35). L. J. S.

**The Crodo Spring at the Juliushall Bath, Harzburg, Harz Mountains.** By ROBERT OTTO and JULIUS TROEGER (*Arch. Pharm.*, 1899, 237, 149—160).—The water was drawn on Sept. 28, 1893, and its temperature was then 9°, and its sp. gr. 1·0110 at 20°. The amount of total solids, directly ascertained, was 1656·2 after drying at 180—190°. The carbonic anhydride really free was 10·031 (=5·074 litres per 100 kilos. at 0° and 760 mm.); the so-called free carbonic anhydride, namely that actually free together with that combined with the carbonates to form hydrogen carbonates, was 16·024 (=8·105 litres). The other constituents, arranged in the conventional manner, were, in parts per 100,000,

SiO <sub>2</sub> .	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .	CaCO <sub>3</sub> .	CaSO <sub>4</sub> .	KBr.	KCl.	NaNO <sub>3</sub> .	Na <sub>2</sub> SO <sub>4</sub> .
1·680	0·074	13·445	39·59	0·196	20·885	0·510	57·63
NaCl.		MgCl <sub>2</sub> .	NH <sub>4</sub> Cl.	FeCO <sub>3</sub> .	Total.		
1487·7		31·36	0·033	0·204	1653·3		C. F. B.

### Physiological Chemistry.

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Permeability of Animal Membranes to Gases in Solution.  
By LEONARD HILL and H. E. RIDWOOD (*Proc. Physiol. Soc.*, 1899, 13—19).—The lung of a frog or toad, with the bronchus tied, sunk in soda water by a weight, is soon filled out with carbonic anhydride, and rises with the weight to the surface; the gas is then discharged, and the lung sinks, when the phenomenon is repeated. This will go on for a week or more, and does not depend on the vitality of the lung,

for a scalded lung acts as well. If the lung is first turned inside out, it does not occur, but in the case of skin, an inside-out bag blows out quickest; this does not happen with oxygen. India-rubber bags behave very similarly. Experiments with other gases are also described.

W. D. H.

**Comparative Physiology of Digestion. III. The Function of the so-called Liver of Molluscs.** By WILHELM BIEDERMANN and P. MORITZ (*Pflüger's Archiv*, 1899, 75, 1—86).—The observations recorded were made principally on snails. The structure of the digestive gland (so-called liver) shows various kinds of cells, "secretory cells" (Barfurth's ferment cells), which form a secretion which is poured into the stomach. The secretion is acid in reaction, lactic acid being present. It acts principally on carbohydrates, especially cellulose and starch, and thus contrasts forcibly with the secretion in caterpillars, which has no action on cellulose, and only a feeble action on starch. The snail's secretion has only a feeble action on proteids. The digestive gland acts like the liver of vertebrates, storing enormous quantities of carbohydrate material in the form of glycogen; this is contained in cells of the inter-acinous connective tissue, and also, especially in the *Limacidae*, in certain liver cells, termed 'absorption cells,' and 'chalk cells.' Fat is also stored in considerable amount, especially in the "chalk cells." The so-called chalk is calcium phosphate, which is regarded as storage material.

The organ is also the great channel of absorption; little or no absorption occurs in the wall of the alimentary canal.

W. D. H.

**Structure of Cell Protoplasm.** By W. B. HARDY (*Journ. Physiol.*, 1899, 24, 155—210).—It is well known that various structures (net works, granules, &c.), have been described from time to time. The present paper is the first of a series in which the appearances alluded to are subjected to a rigorous investigation with the object of determining whether they are natural or artificially produced by hardening and staining reagents. The general conclusion drawn is that the change produced in colloids by fixatives is a separation of solid particles, which are large molecular aggregates; these are linked together by strands to form an open net with fluid in the meshes. The change produced in protoplasm is similar. The change which occurs in cells *post-mortem* or *sub-mortem* (coagulation) is of the same nature.

W. D. H.

**Glycogen in the Frog at Different Seasons.** By J. ATHANASIU (*Pflüger's Archiv*, 1899, 74, 561—569).—There is a small quantity of glycogen in the frog's body during the summer, and the amount is then at the minimum; the maximum occurs in the autumn, and the amount in the spring is also fairly high. By experimental warmth (summer temperature), a lessening of the total glycogen also occurs. The glycogen found at the conclusion of the winter sleep is merely the remainder of the stored material, very little of which would be used during hibernation.

W. D. H.

**Creatinine.** By EMIL WÖRNER (*Zeit. physiol. Chem.*, 1899, 27, 1—13).—Some fragmentary observations by the author confirm

Toppelius and Pommerehne's conclusions, and lead to the belief that Johnson's work on creatinine (Abstr., 1888, 506 ; 1889, 165 ; 1893, i, 55) is faulty ; creatinine prepared from various sources appears to have the same characters ; in other words, there are not several creatinines as Johnson stated. The amount of creatine in muscle is far in excess of creatinine as the older authors stated ; this also is contrary to Johnson's statement. W. D. H.

**Melanins.** By WALTER JONES (*Amer. J. Physiol.*, 1899, 2, 380—393).—A full account of experiments a preliminary notice of which has already been published (this vol., i, 396). W. D. H.

**Toxalbumin from the Common Eel.** By ELOPHE BÈNECH (*Compt. rend.*, 1899, 128, 833—836).—The flesh of the common eel contains a toxalbumin, which, when injected into the vein of the ear of a rabbit, in the proportion of 0.02 gram per kilogram of body weight, causes paralysis, followed by death in about six hours, the blood being dark coloured and partially coagulated. It is precipitated by ammonium sulphate, but not by magnesium sulphate. Acetic, hydrochloric, sulphuric, and nitric acids produce a slight turbidity, soluble in excess, but alkalis have no action ; alcohol produces an abundant coagulum. The substance gives the biuret reaction, and reactions with tannin, platinic chloride, and the reagents of Tanret, Esbach, Méhu, and Millon. It contains C, 50.18 ; H, 7.88 ; N, 16.1, and when dried is a yellowish-white powder with a disagreeable taste and an acrid after-taste. An eel of 600 grams weight yields from 2 to 2.5 grams of the toxalbumin. C. H. B.

**Leucomaines of the Brain.** By WL. GULEWITSCH (*Zeit. physiol. Chem.*, 1899, 27, 50—82).—The fresh brain of the ox does not contain neurine ; choline is found even in aqueous extracts, but by treatment of the alcoholic extract with sodium ethoxide, the quantity obtained is very largely increased. The aqueous extract of brain contains minute quantities of two other basic substances which have not been identified, and also urea in amount greater than can be accounted for by the blood left in the tissue. After saponification of the alcoholic extracts of the brain, the only organic base obtained was choline.

Regarding the separation of organic bases, much stress is laid on the solubilities of their double salts. W. D. H.

**The Proteids of the Thyroid Gland.** By AD. OSWALD (*Zeit. physiol. Chem.*, 1899, 27, 14—49).—The principal proteid of the thyroid gland, the one to which the iodine is linked and to which extracts of the gland owe their action, is a globulin ; it is called thyreoglobulin, and contains 1.6 per cent. of iodine. A nucleo-proteid is also present. The colloid consists of these two proteids.

In thyreoglobulin, artificial pancreatic digestion leads to the formation of tyrosine without any liberation of iodine ; the iodine is therefore not united to the tyrosine group. By heating thyreoglobulin with 10 per cent. sulphuric acid, Baumann's iodothyryn was obtained ; this is free from phosphorus. W. D. H.

**Hæmatin from Blood and the Varieties derived from Various Species of Animal.** By PAUL CAZENEUVE and P. BRETEAU (*Compt. rend.*, 1899, 128, 678—680).—Defibrinated blood is heated to boiling with its own weight of sodium sulphate; the coagulum produced is washed with hot water, and triturated with a warm 1 per cent. alcoholic solution of oxalic acid, this treatment being repeated until the residue is decolorised. The filtered extract is almost neutralised with ammonia; the precipitated hæmatin, after collecting and washing with cold alcohol, is redissolved in dilute ammonia (5 per cent.), and again precipitated by acetic acid, washed with cold water, alcohol, and ether, and finally dried at 135°. By this process, 1 gram of hæmatin is obtained from a litre of blood. Specimens of hæmatin prepared in this way from the blood of the horse, ox, and sheep show differences in composition which indicate that they are distinct chemical species.  
G. T. M.

**Motor Reactions and Laws of Chemotaxis in Paramœcium.** By HERBERT S. JENNINGS (*Amer. J. Physiol.*, 1899, 2, 311—341, 355—379).—The sensibility of *Paramœcium* has been much over-estimated; it is at the bottom of the psychological scale, and simple irritability will account for all its movements. It has a single motor reaction to all stimuli; the direction in which it turns is a matter of chance. The motor reaction in chemotaxis does not differ from other motor reactions. The direction of motion has no relation to the part of the animal stimulated. *Paramœcia* collect in solutions having a weak acid reaction, or in solutions of salts in which the anion is especially active. Negative chemotaxis depends chiefly on the chemical nature of the stimulating substance, not on its injuriousness. Alkaline solutions, and those containing the kations of alkali or earth alkali metals, repel. The repellent power decreases as the atomic weight increases, except that potassium salts are throughout more repellent than sodium salts.  
W. D. H.

**Absorption from the Peritoneal Cavity.** By LAFAYETTE B. MENDEL (*Amer. J. Physiol.*, 1899, 2, 342—351).—A full account of experiments a preliminary notice of which has been previously published (this vol. ii, 309).  
W. D. H.

**The Cause of the High Value of the C/N Quotient in Normal Urine.** By FRITZ PREGL (*Pflüger's Archiv*, 1899, 74, 87—109).—The quotient C/N in the normal urine of men and dogs is greater than in urea; the urine must therefore contain some organic substance or substances which are poorer in nitrogen than is urea. The principal substance is believed to be the hydroxyproteic acid of Bondzynski and Gottlieb.  
W. D. H.

**Excretion of Uric Acid.** By ALEXANDER HAIG (*J. Physiol.*, 1899, 24, 155—157).—Critical remarks on work recently published by Bain and Edgecombe, and by Hopkins and Hope. The main point urged is that correct conclusions cannot be drawn as to the excretion of uric acid unless means are taken to render that substance soluble in the body juices; otherwise it accumulates.  
W. D. H.

**Action of Iodine and Iodine Compounds.** By R. HEINZ (*Virchow's Archiv*, 1899, 155, 44—97).—Iodine injected into the

serous cavities sets up an adhesive form of inflammation, necrosis of the tissues, and increased diapedesis of the blood corpuscles.

Of the chloride, bromide, and iodide of sodium, the last named is the most powerful. The chlorate, bromate, and iodate act as oxidising agents, but only the first-named produces methæmoglobin. Special attention was paid to the activity of sodium iodide; it produces an increase in the leucocytes, and of lymph-formation. Binz's theory that the action is mainly due to the liberation of iodine is accepted.

W. D. H.

**Administration of Suprarenal Extract by the Mouth in Health and Disease.** By O. F. F. GRÜNBAUM (*Proc. Physiol. Soc.*, 1899, 24—25).—In health, administration of suprarenal tabloids by the mouth produces no rise of blood pressure, because the extract is not absorbed quickly enough; this renders it a good hæmostatic, especially in cases of hæmorrhage from the walls of the alimentary canal and bladder.

W. D. H.

**Intravenous Injection of Pituitary Extract.** By EDWARD ALBERT SCHÄFER and SWALE VINCENT (*Proc. Physiol. Soc.*, 1899, 19—21).—The infundibular part of the pituitary contains substances, two in number, which produce effects on blood pressure. These substances dialyse through parchment paper, and are present in decoctions or glycerol extracts. One causes a constriction of arterioles and a rise of blood pressure; the other produces a fall of arterial pressure, which is not abolished by atropine.

W. D. H.

**Excretion of the Constituents of Urine in Fever.** By WACŁAW VON MORACZEWSKI (*Virchow's Archiv*, 1899, 155, 11—43).—Numerous constituents of the urine were estimated in the several stages of different cases of fever, and the results are given in fullest detail. The general results are in the main confirmatory of earlier investigations. Some importance is attached to the observation that in an early stage of a fever the amount of chlorine in the urine rises, and that of phosphorus falls; the reverse occurs later on.

W. D. H.

**Action of the Pancreas on the Diphtheric Toxin.** By ALBERT CHARRIN and LEVADITI (*Compt. rend.*, 1899, 128, 839—841).—Experiments are described showing that the pancreas or its secretions exert a distinct attenuating influence on the diphtheric toxin, and that this effect is probably due to some diastatic action.

C. H. B.

**Fat in the Animal Body under the Influence of Phosphorus.** By J. ATHANASIU (*Pflüger's Archiv*, 1899, 74, 511—560).—The absolute quantity of fat in the animal organism undergoes no change under the influence of phosphorus, but in phosphorus poisoning there is a migration of fat to the liver. The only substance which is quantitatively altered is glycogen, the amount of which is lessened, especially in the liver.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

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**Fermentation of Galactose.** By DIENERT (*Compt. rend.*, 1899, 128, 569—571).—When yeasts which are generally regarded as active in producing the fermentation of galactose are grown in different portions of the same nitrogenous culture fluid containing in one part (A) some saccharose, and in the other (B) some galactose, and the yeasts, after being washed, are placed in a 10 per cent. solution of galactose, it is found that the yeast B is much more active in producing fermentation than the yeast A. After each of them has once fermented a galactose solution, however, they become equal with respect to galactose, but show differences if put back into a solution of glucose. Conditions that promote propagation accelerate the rate at which the yeast becomes acclimatised, so to speak, in solutions of galactose. Some yeasts, such as *Saccharomyces Ludwigii*, do not appreciably ferment galactose, even when grown in a highly nitrogenous liquid containing glucose as well as galactose. Imperfect fermentation is produced when the proportion of yeast is very large. The fermentation of galactose requires conditions which are not necessary in the case of glucose (compare Dubourg, this vol., ii, 376). C. H. B.

**Fermentation of Galactose.** By DIENERT (*Compt. rend.*, 1899, 128, 617—618).—A specimen of yeast, which does not ferment lactose, is cultivated in a nutritive medium in the presence of saccharose and lactose, and afterwards washed and placed in a 10 per cent. solution of galactose. The yeast is not acclimatised to galactose, and fermentation is set up only after 2—3 days. A similar result is obtained when the yeast is cultivated in the presence of saccharose alone. The same yeast, acclimatised to galactose, after cultivation in presence of an unfermentable sugar, lactose for example, partly loses its activity towards galactose, for when placed in a solution of this sugar it sets up fermentation, but only decomposes a portion of the carbohydrate. When cultivated in presence of a fermentable sugar, this loss of activity is not noticed. A yeast, such as *Saccharomyces Ludwigii*, which is only feebly active towards galactose, entirely loses this activity when macerated with a solution of lactose.

On the other hand, yeasts which ferment lactose, when cultivated in a medium containing this sugar, readily ferment galactose, but when macerated in a solution of saccharose, they lose this activity and only set up fermentation in solutions of galactose after 1—2 days. By treating the yeast in a manner similar to that employed by Hill (*Trans.*, 1898, 73, 634), an enzyme, lactase, may be isolated which hydrolyses lactose into glucose and galactose; this explains the fact that a yeast capable of fermenting lactose when cultivated in the presence of this sugar is already acclimatised to galactose.

G. T. M.

**Stimulating Action of Pancreas on Alcoholic Fermentation.** By RAPHAEL LÉPINE and MARTZ (*Compt. rend.*, 1899, 128, 904—906).—Portions of the pancreas of the dog are digested for 5 minutes with

boiling water to remove trypsin, and placed in flasks containing sugar, Pasteur's "mineral solution," and beer yeast. It is found that the addition of pancreas increases the amount of fermentation taking place in a given time; in each case, two experiments were made, one with normal pancreas, and the other with pancreas which had been recently excited by the electrical stimulation of the nerves surrounding the pancreatico-duodenal artery. The amount of fermentation is greater in the latter experiment, and the amount of carbonic anhydride produced for each gram of sugar destroyed is proportionately greater. This result is attributed to the peptones present in pancreas, and especially in the recently stimulated organ. Pancreas macerated for 30 minutes with water at 40° contains a large amount of peptones, and the accelerating effect on the fermentation attains a maximum, but when the maceration is prolonged for 2 hours at the same temperature, the action is greatly diminished. Concordant results can only be obtained with freshly excised pancreas in which trypsin has been destroyed in the manner indicated.

G. T. M.

**Molecular Relations of Solutions of Tetanus Poison.** By W. G. RUPPEL and F. RANSOM (*Zeit. physiol. Chem.*, 1899, 27, 109—113).—Nutritive fluids were investigated by the Raoult-Beckmann method, before and after the growth of tetanus bacilli in them. Those infected with the growth showed a greater depression of the freezing point. This must indicate an increase in the number of molecules. Some media, when kept for a long time, lost some of their toxic characters; the determination of the lowering of the freezing point indicated that molecular condensation accompanied this. The amount of solid residue throughout was practically unaltered.

W. D. H.

**Direct Conversion of Ammonia in Solution into Nitrates.** By E. DEMOUSSY (*Compt. rend.*, 1899, 128, 566—599).—When a solution containing ammonium sulphate, calcium carbonate, and potassium phosphate is inoculated with soil containing the nitrous and nitric ferments, the ammonia is converted into nitrate, but the intermediate formation of nitrite is readily detected. If, however, the nitric ferment is first cultivated in a solution of potassium nitrite, calcium carbonate, and potassium phosphate, and then an ammonium salt is added to the liquid, the ammonia is completely and somewhat rapidly converted into nitrate, but the intermediate formation of nitrite cannot be recognised at any stage. It would seem, therefore, that the impossibility of detecting nitrites in soils in which nitrification is going on is due to the fact that the rates of production of nitrite and of its conversion into nitrate are equal. This conversion is made possible by the slow rate of production of ammonia from the organic matter in the soil and the consequent slow production of nitrite, whilst, on the other hand, the quantity of nitric ferment present is large. In liquids containing ammonia salts, the production of nitrites is rapid and the number of nitric organisms present is proportionately much smaller than in soils.

C. H. B.



**Reducing Action of Denitrifying Bacteria.** By G. AMPOLA and C. ULPANI (*Gazzetta*, 1899, 29, i, 49—72. Compare Abstr., 1898, ii, 622).—Denitrifying bacteria do not attack asparagine or nitromethane, and with ethylic nitrate the action is very slow. From this, it is concluded that denitrification only takes place with oxygen compounds of nitrogen, and only with such of these as are electrolytes, and are thus dissociated into ions in solution.

From the results of a number of experiments, the authors find it necessary to modify Weissenberg's classification of denitrifying bacteria, and to arrange them under three heads: 1. Those which destroy nitrites but not nitrates, namely, *Bacterium denitrificans* I. of Burri and Stutzer. 2. Those destroying nitrates but not nitrites—*Bacillus pyocyaneus* and *Bacterium denitrificans* V. 3. All other denitrifying bacteria, which attack both nitrites and nitrates.

The qualitative and quantitative examination of the action of *B. denitrificans* V. on a number of metallic nitrates show that those of lithium, ammonium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, and barium are denitrified, whilst the nitrates of silver, thorium, yttrium, iron, manganese, and aluminium are not attacked; and that the more electropositive the metal and the lower its atomic weight, the more rapidly does denitrification take place. Carbamide nitrate, which is only slightly dissociated in solution, is slowly attacked, whilst with the nitrates of strychnine, brucine, cocaine, and pilocarpine, which are entirely ionised in solution, denitrification is soon complete. The bacteria do not develop in metallic chromates, and only to a small extent in bromates or iodates; chlorates, arsenates, and ferricyanides suffer reduction, but sulphates, phosphates, and molybdates remain unchanged.

T. H. P.

**An Oxydase secreted by *Bacillus Coli* which can produce Pigments.** By GABRIEL ROUX (*Compt. rend.*, 1899, 128, 693—695).—*Bacillus coli* cultivated on artichoke gives rise to an intense green coloration. Laccase develops an olive-green coloration with a decoction of artichokes. When *B. coli* is cultivated in a medium containing quinol, a brown coloration is developed. These experiments indicate that *B. coli* secretes an oxydase which produces colorations in the presence of easily oxidisable substances.

G. T. M.

**Dextrin considered as Reserve Material.** By LECLERC DU SABLON (*Compt. rend.*, 1899, 128, 944—945).—The quantity of starch in the hyacinth bulb during the stage of growth (January to March) is relatively small. It attains a maximum in the quiescent stage (May), and falls to a minimum when the reserve material is being utilised (November to February). If dextrin is an intermediate product in the formation of starch, it should be found in the bulb during the growing stage; if it is also a result of the assimilation of starch, it should still be found when the reserves are being utilised; this is shown to be the case, but the maximum amount of dextrin is present during the quiescent stage, hence it appears to play the part of a reserve material quite independently of starch. This conclusion is borne out by a study of the reserve materials in the bulbs of the tulip

and lily, both of which contain the maximum amount of dextrin during the resting stage. G. T. M.

**Sugar of Orange Peel.** By JULIAN FLATAU and HENRI LABBÉ (*Bull. Soc. Chim.*, 1898, [iii], 19, 408).—When fresh orange peel is extracted with water or alcohol, a small quantity of a gummy, uncrystallisable sugar is obtained, which appears to be identical with mannose, since it forms a phenylhydrazone crystallising in golden-yellow needles and melting at 199—200°, is precipitated by lead acetate in neutral solution, and does not restore the colour of rosaniline decolorised by sulphurous acid. N. L.

**Progressive Development of Grape Clusters.** By AIMÉ GIRARD and LINDET (*Bull. Soc. Chim.*, 1898, [iii], 19, 585—588).—This is a *résumé* of a memoir shortly to be published in the *Bulletin du ministère de l'Agriculture*. A series of analyses of three varieties of French grapes was made at various stages of growth. The weight of the stalks is found to be nearly constant throughout, the only changes in composition noted being a slight loss of moisture as ripening proceeds and an occasional accumulation of sugars and acids in their passage through the vessels. The increase in weight of the grape during maturation is due to the growth of the pulp alone, the skin remaining constant, and the seeds suffering a diminution in weight. With regard to the pulp, the process of ripening is marked by a gradual increase in the sugars (consisting of equal quantities of lævulose and dextrose, probably accompanied by cane sugar in the early stages) and in the combined tartaric acid, a decrease in the amount of free acids, which include tartaric, malic, and glycollic acids, and a large increase in the nitrogenous and mineral constituents, especially in the later stages. At the commencement of growth, the zone of pulp surrounding the seeds is richer in sugar and poorer in acids than the exterior portions, but as ripening proceeds this condition is reversed. Notwithstanding its increase in size, the weight of the skin is practically constant; water, however, is lost, and new materials are assimilated. The combined tartaric acid first increases and then rapidly diminishes; the free acids tend to disappear before ripening; and the tannin, which is accompanied by its anhydride phlobaphen, first increases and then remains constant in amount. The odorous matter, to which the bouquet is due, is developed in the later stages of growth. The amount of cellulose, nitrogenous substances, and mineral matter contained in the seeds remains constant almost throughout. The same applies to the combined weight of the tannin and phlobaphen, although the relative proportions of these two compounds vary considerably. The gradual decrease in weight of the seeds is due to loss of water and of oil. In the last stages of ripening, there is a more abundant formation of volatile fatty acids, which exist partly in the free state and partly as glycerides, and at the same time a corresponding decrease in the nitrogenous substances, mineral matter, and cellulose. N. L.

**Phlobaphen of the Grape.** By AIMÉ GIRARD and LINDET (*Bull. Soc. Chim.*, 1898, [iii], 19, 583—584).—Further study of the bitter, resinous substance shown by the authors (*Bulletin du ministère de l'Agriculture*, 1895, 694) to be present in the stalk, skin, and stones

of the grape has established its identity with phlobaphen, which Etti (Abstr., 1878, 797; 1883, 995) obtained from oak bark and from hops, and considered to be an anhydride of tannin of the composition  $C_{34}H_{30}O_{17}$ . On boiling the acid solution of the stalks or stones from which the phlobaphen has been isolated, a red substance is deposited which closely resembles phlobaphen in composition and properties, and is similar to the insoluble red compounds usually found in association with tannin; the formation of reducing sugars under these conditions was not observed. Estimations of the tannin and phlobaphen in grape stalks show that the sum of the amounts of the two compounds is constant, a decrease in the one being compensated for by an increase in the other, and it is suggested that phlobaphen is the reserve material in which tannin is stored in the plant. N. L.

**A Phlobaphen from Grape Seeds.** By LIVIO SOSTEGNI (*Gazzetta*, 1899, 29, i, 143—149. Compare Abstr., 1898, i, 331).—The seeds of red grapes were washed with water, dried in the air, and kept in a dry place for about a year. On digesting with water at 50—60° and adding hydrochloric acid, a yellowish substance was precipitated which, in the moist state, is very soluble in alcohol, less so in water, and is only slightly dissolved by ether. The aqueous solution gives with iron salts a bluish-green precipitate, and is coloured brown by potassium dichromate; salts of copper, lead, zinc, &c., also precipitate it, the zinc compound being soluble in acetic acid, but insoluble in ammonia. On drying in the air, this substance gradually acquires a brownish colour, becomes absolutely insoluble in all ordinary solvents, and acquires all the properties of the phlobaphen obtained by the author from red wine (*loc. cit.*). It can, however, be re-dissolved in hot glycerol, from which dilute hydrochloric acid precipitates it in a form almost insoluble in water, but soluble in alcohol, giving a deep ruby-red solution.

Solutions of this reprecipitated substance show an absorption band beginning at about the D lines and extending over the rest of the spectrum to the violet. The mean of two determinations give its percentage of carbon as 58.55, and of hydrogen 4.98. On fusion with potash, it yields phenol, catechol, and possibly phloroglucinol. Its copper compound contains 29.48 per cent. of metal, and its silver salt 50.92 per cent. It forms a brominated derivative containing 41.2 per cent. of halogen. The addition of alcoholic potash to an alcoholic solution of the substance precipitates a dark brown substance which is very soluble in water and absorbs oxygen from the air very rapidly.

From all these reactions, the author concludes that the substance obtained from grape seeds is identical with the colouring matter of the grape itself. T. H. P.

**Mercury in the Products from Vines treated with Mercurial Dressings.** By LÉO VIGNON and J. PERRAUD (*Compt. rend.*, 1899, 128, 830—832).—When vines have been dressed with mixtures of copper sulphate, lime, and mercuric chloride in proportion not exceeding 1 gram per litre, the quantity of mercury found in the wine, lees, or other products does not exceed 2 or 3 milligrams per litre or per kilo., and is generally much less, besides being mainly in an insoluble form. It follows that it is not at all likely to be injurious.

On the other hand, the application of the mercurial dressing is found to be distinctly injurious to the plant. C. H. B.

**Analyses of Pomegranates.** By ARTHUR BOENTRÄGER and G. PARIS (*Bied. Centr.*, 1899, 28, 198—200; from *Zeits. Unters. Nahrungs-u. Genussmittel*, 1898, 158).—Analyses of the expressed juice of six kinds of pomegranates showed that in the case of ripe fruit the juice contained 0·37—0·51 gram of acid and 10·50—13·69 grams of reducing sugar per 100 c.c., whilst unripe fruit contained acid 3·04 and 3·36, reducing sugar 7·81 and 11·33 per cent. The musts were normally fermented, and an orange-red wine obtained resembling raspberries in taste. Even the ripe fruit contains so little sugar that only wines can be obtained which contain low percentages of alcohol. The amounts of alcohol actually found in three samples were 4·37, 5·72, and 6·99 grams per 100 c.c. N. H. J. M.

**Currant Bushes failing to bear Fruit. Investigation into the Cause—Analyses of the Soil.** By ANDREW P. AITKEN (*Trans. Highland and Agric. Soc. of Scotland*, 1898, [v], 10, 293—299).—In an orchard near Glasgow it was observed during four seasons that whilst the currant bushes seemed healthy and flowered abundantly, the flowers soon dropped off, with the result that no fruit was produced. Analyses of the soil showed that the soil and subsoil contained fair amounts of nitrogen and phosphoric acid, but were poor in potash and lime. Application of large amounts of lime and potash had, however, no effect. It is concluded that the injury is due to some substance present in the air during the flowering period.

Comparison of the soil of the orchard, which had been heavily dunged, with that of the adjacent arable land showed less difference in the percentages of organic matter and nitrogen than might be expected. In the amounts of available potash and phosphoric acid, however, great differences were found, the available potash being increased three-fold and the amount of available phosphoric acid being doubled in the first six inches of soil under the influence of farmyard manure. The total potash and phosphoric acid were not greatly increased. N. H. J. M.

**Amount of Lignin in the Wood of Trees with Acicular Leaves.** By ADOLF CIESLAR (*Bied. Centr.*, 1899, 28, 250—251; from *Mitt. forstl. Versuchsw. Oesterr.*, 1897, Heft. 23).—Estimations of lignin by Zeisel's methoxyl method (Benedikt and Bamberger) furnished results from which the following conclusions are drawn.

The amount of lignin in the single species varies more than in the case of different coniferous woods. Of the woods examined, that of spruce fir contained the least lignin (39·10 per cent.); that of silver fir the most (45·50 per cent.); whilst pine wood contained 43·81 per cent. In pine wood, the amount of lignin decreases from the base upwards, and the old wood contains more lignin than the newer wood.

Wood which has grown quickly contains less lignin, in a given volume, than wood which has grown slowly. The conditions favourable to the production of lignin are presence of suitable plant-food and abundance of light. N. H. J. M.

**Feeding Experiments, 1897.** By ANDREW P. AITKEN (*Trans. Highland and Agric. Soc. of Scotland*, 1898, [v], 10, 259—292).—*Cattle fed at Mains of Laithers* (compare *ibid.*, 1897, 156—180).—The experiments, which were similar to those of 1896, and extended over 16 weeks, were made with 50 cattle, divided into five lots of five pairs; they were weighed every four weeks. Each pair received swedes (17,920 lbs.) and straw, and, in addition, those of Lot 1 had 1492 lbs. of decorticated cotton-cake and dried grains (mixed); those of Lot 2, linseed cake meal (1120 lbs.); those of Lot 3, barley bran (1680 lbs.); Lot 4, ground barley (1232 lbs.), and Lot 5, ground maize (1491 lbs.). The amounts actually consumed and the increase in live weight of each pair are given in tables. The greatest increase was obtained in Lots 1 and 2, which (if one bullock which made no progress is excluded) were about equal; Lots 3 and 5 consumed about the same amounts of digestible organic matter (Lot 3 had, however, the most proteids) and made equal progress, although Lot 3 were fat before the end of the experiment, whilst Lot 5, which had grown, required two months longer. Lot 4 gave much the least satisfactory results. The results show that the nutritive ratio of a food (especially of a mixed food) is a very imperfect guide, and also illustrate the difficulties which arise from the individual characters of cattle as feeders, even when a considerable number are employed in experiments of this kind.

*Sheep-feeding Experiments at Ferney Castle and Whitelaw.*—Four lots of 20 sheep each were fed at each farm during about 12 weeks on turnips (*ad lib.*), with 1 lb. per head per day of (1) decorticated cotton-cake and dried brewers' grains (equal parts); (2) linseed cake; (3) bruised oats and barley (equal parts); and (4) bruised oats and maize (equal parts).

The results showed that there is very little difference in the effect of linseed cake and a mixture of cotton cake and brewers' grains when consumed with turnips. Oats and maize proved to be slightly better than oats and barley, both mixtures being much inferior to cake; and the more highly nitrogenous food is more favourable to wool production. In both farms, most tallow was produced under the influence of the oats and maize mixture; this had also been observed in a former experiment.

N. H. J. M.

**Maize Oilcake for Milch Cows.** By BERNHARD SCHULZE (*Bied. Centr.*, 1899, 28, 165—167; from *Fühling's Landw. Zeit.*, 1898, ii, 12).—The average percentage composition of maize oilcake was found to be as follows:

Water.	Proteids.	Fat.	N-free extract.	Crude fibre.	Ash.
10.28	19.46—26.91	8.10—16.18	38.97—43.10	10.26	2.37

Feeding experiments with twelve cows showed a slight increase in the yield of milk with 2—4 lbs. of the cake, but the percentage of milk-fat was diminished. The cows, however, gained in weight, and it is probable that the cake may be employed with advantage for fattening.

N. H. J. M.

**Carbon in Humic Substances.** By GUSTAVE ANDRÉ (*Compt. rend.*, 1899, 128, 513—516).—The author has continued his researches (this vol., ii, 119) with special reference to the relation between carbon and nitrogen. The results are summarised in the following table, I being the ratio C/N, II carbon per cent. of the initial carbon.

	Peat.		Cultivated soil.		Moorland soil.		Vegetable mould.	
	I.	II.	I.	II.	I.	II.	I.	II.
<i>Treatment with potassium hydroxide.</i>								
Insoluble portion.....	147·6	24·5	84·4	40·0	82·4	35·4	40·4	41·8
Soluble portion { precipitated by acids .....	26·9	44·8	16·6	23·0	27·1	36·6	10·8	18·7
{ not precipitated by acids.....	17·7	30·7	9·8	37·0	16·7	28·0	10·1	39·5
<i>Treatment with acid.</i>								
Soluble portion .....	40·7	82·2	33·6	76·3	48·8	75·6	17·7	82·6
Insoluble portion.....	9·4	17·8	6·6	23·7	11·9	24·4	8·5	17·4

Peat and moorland soil, which are acid soils, differ markedly from cultivated soil and vegetable mould in the composition of the soluble products of the action of potassium hydroxide. Hydrochloric acid breaks down the organic matter less readily than potassium hydroxide. In both cases, the ratio C/N is lower and the degree of condensation is less the more soluble the product. Cultivated soil and vegetable mould, with either alkali or acid, yield soluble products which have the composition of simple amides.

C. H. B.

**Action of very Dilute Acids on Phosphates of the Soil.** By TH. SCHLESING, jun. (*Compt. rend.*, 1899, 1004—1007).—If specimens of a soil containing phosphates are treated with very dilute nitric acid, it is found that, up to a certain point, the amount of phosphate dissolved varies with the concentration of the acid. Beyond this, a further addition of acid does not increase the amount of phosphate in solution, and it is only when the concentration is considerably increased that the quantity of soluble phosphate is appreciably augmented. The phosphates of calcium, magnesium, and the alkali metals are dissolved out during the first stage, and the extract contains only traces of iron; in the second stage, however, the solution contains a notable amount of iron. These experiments were made on soils from four different localities, and the results are tabulated so as to indicate the relationship between the strength of acid employed, the final acidity of the extract, and the amounts of phosphoric acid and ferric oxide which have passed into solution.

G. T. M.

**Explanation of Denitrification and of the Diminution of Crops after the Application of Fresh Farmyard Manure.** By W. KRÜGER and W. SCHNEIDEWIND (*Bied. Centr.*, 1899, 28, 154—156; from *Deut. Landw. Presse*, 1897, No. 92, 832).—From the

results of two series of pot experiments, it was concluded that the diminished yield following manuring with fæces and straw depends on a purely mechanical action, or else that the solid substance influences the microbes in the soil by increasing the porosity of the soil, or by supplying nutritive matter. Further experiments in the laboratory showed that the action is physiological, and not mechanical, and is due mainly to the presence of xylan in the straw. It is probable that denitrification can only take place in presence of xylan or similar substances. The introduction of denitrifying organisms by application of manure containing straw is not of importance, since the microbes are already in the soil in sufficient numbers, and may also be introduced along with seed, or from the air. Their activity, however, depends on the presence of suitable nutritive matter.

THEODOR PFEIFFER (*Deut. Landw. Presse*, 1897, 911) considers the above conclusions premature, and that whilst it is recognised that straw and fæces act as sources of food for denitrifying organisms rather than as carriers of the microbes, it is doubtful whether xylan is a good source of carbon for them.

N. H. J. M.

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## Analytical Chemistry.

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**An Automatic Burette.** By HENRY DROOP RICHMOND (*Analyst*, 1899, 24, 2—4).—This burette is intended for the delivery of strong sulphuric acid. The lower end is fitted with a three-way tap which is connected with the stock bottle by means of a siphon and the usual air-trap, which enables an india-rubber connection to be used.

The burette is closed by a cork, fitted with a very narrow tube which reaches to the zero point and the protruding part of which rises nearly to the top of an air chamber, the lower part of which is connected with a narrow ascending tube made to dip into a small funnel passing through the cork of the stock bottle.

When the burette wants filling, the tap is turned half-round. The liquid then siphons over from the stock bottle, fills the burette to the zero division, and, running over into the air chamber, ascends the tube until its level is equal to that of the stock bottle. When the liquid is run out from the burette, air is drawn down the ascending tube and bubbles through the liquid in the air chamber, and when the burette is refilled the acid in the air chamber is forced back into the stock bottle.

L. DE K.

**Automatic Burettes.** By ALFRED W. STOKES (*Analyst*, 1899, 24, 4—6).—Two automatic burettes are described, of which the more accurate form consists essentially of a measuring vessel having a lateral opening at the top and another at the bottom. The lower end, connected with the supply, revolves in a sleeve, and the upper end, connected with the overflow, revolves in another. The instant the vessel is revolved, all connection with the reservoir and overflow is cut



off, so that the measure contains an absolutely exact quantity of liquid. Half a revolution brings the lower opening to the exit tube, and its upper opening to an air inlet. L. DE K.

**Rapid Estimation of Small Quantities of Free Phosphorus in Phosphorus Paste.** By LESTER REED (*Analyst*, 1899, 24, 33).—A weighed quantity of yellow phosphorus is dissolved in 20 c.c. of carbon bisulphide, and introduced into a bottle containing 1 c.c. of the usual paste (flour, glucose, and water), 5 c.c. of absolute alcohol added, and the whole shaken until the paste is disintegrated. A solution of bromine in carbon disulphide (5 or 10 grams in 50 c.c.) is now added from a burette until a decided yellow colour is obtained in the supernatant liquid.

A weighed quantity of the phosphorus paste is then mixed with 5 c.c. of absolute alcohol, shaken until thoroughly disintegrated, 20 c.c. of carbon bisulphide added, and the titration with the bromine solution conducted as before. The method of calculation is obvious. Part of the phosphorus may have been oxidised to phosphorous acid which also absorbs bromine; its amount is ascertained by extracting the paste with proof spirit and titrating the filtrate. L. DE K.

**Composition of Ammonium Magnesium Phosphate.** By FRANK A. GOOCH and MARTHA AUSTIN (*Zeit. anorg. Chem.*, 1899, 20, 121—136).—When a magnesium salt is precipitated with excess of phosphate solution in the presence of ammonia and ammonium chloride, the precipitate contains more ammonium and less magnesium than the normal salt, and on ignition leaves a residue greater in weight than the normal phosphate. Conversely, when a phosphate is precipitated with excess of magnesia mixture in the presence of ammonia and ammonium chloride, a precipitate of similar composition is obtained, causing a low result for the analysis. The salt which is formed to some extent is probably  $(\text{NH}_4)_4\text{Mg}(\text{PO}_4)_2$ , which, on ignition, yields the metaphosphate  $\text{Mg}(\text{PO}_3)_2$ , and if the excess in weight of precipitate obtained by precipitating a magnesium salt in the ordinary way with excess of phosphate in the presence of ammonia and ammonium chloride is calculated out on this assumption it sometimes corresponds with 10 per cent. of metaphosphate. The results of a large series of precipitations under various conditions are given. Accurate results are obtained in the estimation of magnesium and phosphoric acid, when the precipitate obtained in the ordinary way is allowed to settle, separated from the excess of precipitant by decantation, redissolved in hydrochloric acid, again precipitated with a slight excess of ammonia, and washed with dilute ammonia. Accurate results are also obtained by adding a slight excess of magnesia mixture to the solution of phosphate, which must not contain more than 5—10 per cent. of ammonium chloride, and then adding a slight excess of ammonia. When more ammonium chloride is present, or when more than double the theoretical quantity of magnesia mixture is employed, it is necessary to redissolve the precipitate and again precipitate with a slight excess of ammonia. E. C. R.

**Estimation of Carbonic Oxide.** By ARMAND GAUTIER (*Compt. rend.*, 1899, 128, 487—488).—A question of priority. C. H. B.

**Analysis of Sediment deposited during Electrolytic Refining of Copper.** By AUGUSTE HOLLARD (*Bull. Soc. Chim.*, 1898, 19, [iii], 470—472).—This sediment contains notable amounts of gold, silver, and copper. The gold is estimated by fusing the dried sediment with a mixture of litharge, nitre, sodium carbonate, and borax, a further quantity of litharge and a small amount of carbon being added towards the end of the operation; the lead button produced is cupelled and the resulting silver-gold alloy parted with nitric acid. Another portion of the dried sediment is heated in a current of chlorine until the volatile chlorides of arsenic, antimony, &c., are removed; the residual chlorides are lixiviated with dilute nitric acid, the copper in the filtrate and the silver in the precipitate (the latter after treatment with potassium cyanide) being estimated electrolytically. G. T. M.

**Estimation of Copper and Mercury in Grapes, Wines, Lees, and Marcs.** By LÉO VIGNON and BARRILLOT (*Compt. rend.*, 1899, 128, 613—615).—Solutions of copper and mercury salts are employed as remedies in parasitic diseases of the vine, and traces of these metals are accordingly found in grapes and wine. The wine is filtered, and the lees are extracted with water and cold dilute aqua regia; grapes and husks are also submitted to the latter treatment. The solutions obtained in this way are treated with hydrogen sulphide, the precipitated sulphides digested with hot nitric acid, and the mixture filtered. The copper in the solution is estimated electrolytically, and the mercury in the residue is determined by the authors' colorimetric method (*Abstr.*, 1893, ii, 345). G. T. M.

**Volumetric Estimation of Nickel.** By GIOVANNI GIORGIS (*Gazzetta*, 1899, 29, i, 72—80).—Gibbs' method of estimating nickel, namely, precipitating with an alcoholic solution of oxalic acid of known strength, and by means of permanganate determining either the oxalic acid left in the filtrate, or that contained in the precipitate, is inaccurate, owing, firstly, to the partial solubility of the nickel oxalate, and, secondly, to the fact that the removal of the alcohol from the liquid cannot be completely effected without decomposing some of the oxalic acid. To remove these objections, the author has devised an improved process, which consists in using as precipitant an oxalic acid solution of either barium or strontium oxalate of known strength. No addition of alcohol is necessary, for on boiling the liquid the nickel is thrown down quantitatively as oxalate. The oxalic acid in the filtrate may then be estimated by titrating an aliquot part with permanganate, or that in the precipitate by treating it with a little sodium carbonate or hydroxide, acidifying with sulphuric acid, and titrating with permanganate. Test analyses of nickel sulphate solutions and of nickeliferous steels show that the method gives good results. T. H. P.

**Estimation of the Amount of Softening Agent required for Hard Water.** By LEO VIGNON and MEUNIER (*Compt. rend.*, 1899, 128, 683—686).—Carbonic anhydride in water, whether free or combined as hydrogen carbonate, is readily estimated by titrating the water with standard calcium hydroxide solution mixed with an equal volume

of alcohol containing phenolphthalein (compare Abstr., 1888, 325). From this analysis, the amount of lime required to remove the temporary hardness is readily calculated. The amount of sodium carbonate required to remove the chlorides and sulphates of calcium and magnesium is obtained in a similar manner; the water is titrated with a standard solution of this reagent, an equal volume of alcohol being added to render the precipitation of calcium and magnesium carbonates complete; the indicator employed is phenolphthalein. G. T. M.

**Technical Analysis and Softening of Water for Boilers.** By GIOVANNI GIORGIS and G. FELICIANI (*Gazzetta*, 1899, 29, i, 152—167).—The authors give two volumetric methods for determining the total and permanent hardness of water. In the first, a certain volume of the water is acidified with acetic acid, boiled to expel carbonic anhydride, and neutralised with caustic soda; a known volume of standard sodium phosphate solution is then added, the solution boiled for some minutes, and sodium hydroxide added drop by drop until the liquid is just alkaline. By this means, the lime and magnesia are precipitated as neutral phosphates, and by determining the excess of sodium phosphate added the amounts of lime and magnesia in the water can be calculated.

The other method is a modification of that given by Knöfler (Abstr., 1886, 180). The water is acidified with hydrochloric acid, boiled, and carefully neutralised with sodium hydroxide solution; a known volume of decinormal soda is then added, the solution boiled, decinormal sodium carbonate added, and the boiling continued for some minutes. On cooling, the excess of alkali in an aliquot part of the liquid is determined by titration with decinormal hydrochloric acid. The hardness of the water is calculated from the quantity of sodium hydroxide and carbonate required to precipitate the lime and magnesia. These methods have been tested and found to give good results.

For the softening of water, the authors recommend the combined use of lime and sodium carbonate, and show how, in this way, the calculation of the requisite quantities to be added to any particular water, as given by Kalman's formula, is simplified. The lime is first weighed out and slaked with a small quantity of the water to be softened; when completely slaked, it is added to the remainder of the water, to which after some time the proper quantity of a standard solution of sodium carbonate is added. T. H. P.

**Detection of Saw-dust in Flour.** By A. LE-ROY (*Bull. Soc. Chim.*, 1898, 19, [iii], 478).—The detection of saw-dust in inferior qualities of wheat flour and in oat and barley flour is rendered difficult from the fact that these flours, when unadulterated, contain a certain amount of cellulose (bran) derived from the grain. An intense, crimson-red coloration is developed in the particles of saw-dust when the adulterated flour is treated with a warm alcoholic solution of phloroglucinol containing phosphoric acid; the colour produced in the particles of bran is negligible in comparison. When the alcoholic solution is acidified with hydrochloric acid, the action appears more energetic, but the contrast between the behaviour of the two forms of cellulose is less striking. The saw-dust from deal, birch, oak, and cherrywood

develops this coloration, that from corozo does not. An approximate determination of the amount of adulterant is obtained by using a pure flour, gradually adding known quantities of saw-dust, and matching the coloration developed by phloroglucinol with that of the adulterated specimen.

G. T. M.

**Estimation of Phenol in Urine.** By CARL NEUBERG (*Zeit. physiol. Chem.*, 1899, 27, 123—134).—The method of estimating phenol introduced by Kossler and Penny (*Abstr.*, 1893, ii, 100) was examined, and certain disadvantages are pointed out. It gives too high results in the presence of dextrose. Some modifications are suggested.

W. D. H.

**New Test for Formaldehyde.** By NORMAN LEONARD and HARRY M. SMITH (*Analyst*, 1899, 24, 86).—The violet coloration occasionally observed when milk is heated with strong hydrochloric acid can form a very delicate reaction for proving the presence of formaldehyde. The sample should be heated with about 5 times its volume of hydrochloric acid, which must contain a minute trace of iron, when in the case of milks containing such quantities of formaldehyde as are commonly added a fine violet colour quickly appears, even if the milk contains only 1 part per million of the preservative. If much over 0.1 per cent. of formaldehyde is present, a yellow coloration is obtained, but this will change to violet on addition of a large excess of hydrochloric acid. It is safer to work in the cold, but the coloration then takes a longer time to develop.

L. DE K.

**A Delicate Test for Acetonedicarboxylic Acid.** By GEORGES DENIGÈS (*Compt. rend.*, 1899, 128, 680—682).—This acid, like other aliphatic ketones, forms a compound with mercuric sulphate. This substance has the formula  $\text{Hg}_3\text{SO}_6 \cdot 2\text{CO}(\text{CH}_2 \cdot \text{COO})_2\text{Hg}$ , and is obtained as a white precipitate when excess of mercuric sulphate solution is added to a solution of acetonedicarboxylic acid; its formation is readily observed even when the ketonic acid is present only in traces, and may be employed to detect as little as 1 milligram of this substance per litre. The time which elapses between the addition of the reagent and the appearance of the turbidity is also an indication of the quantity of acetonedicarboxylic acid present in the solution, and a table is given showing the connection between the interval of time and the quantity of the acid in centigrams per litre.

G. T. M.

**Estimation of Malic Acid in Grapes.** By AIMÉ GIRARD and LINDET (*Bull. Soc. Chim.*, 1898, [iii], 19, 585).—After removal of the free and combined tartaric acid by addition of alcohol and ether and precipitation with potash, according to Berthelot and Fleurieu's process, the liquid is evaporated to remove alcohol and ether, the residue dissolved in water, the solution boiled, and normal lead acetate added until a slight opalescence is produced. The solution is filtered while hot, and the lead malate, which crystallises on cooling, is collected, dried, and weighed. Further quantities of lead malate are obtained by repeated treatment of the mother liquor, the acidity of

which is finally determined, and a correction applied for the lead malate remaining in solution, according to the table given below :

Free acetic acid per 100 c.c. }	0.21	0.40	0.55	0.73	0.90
mother liquor..... }					
Lead malate dissolved in }	0.10	0.13	0.16	0.18	0.20
100 c.c. mother liquor ... }					

N. L.

**Analysis of Gallotannic Acids.** By ADOLF HEINEMANN (*Zeit. angew. Chem.*, 1899, 245—253).—An elaborate investigation of the merits of the gravimetric and volumetric methods for the estimation of tannin.

The conclusions arrived at are that, either from a scientific or a technical point of view, the gravimetric method should be accepted and the volumetric one rejected. The first, as is well known, consists in evaporating a portion of the infusion and weighing the residue; this operation is then repeated after removing the tannins by means of hide-powder. But even this process gives untrustworthy results unless worked under strictly comparable conditions; the author now proposes the following modification: To 100 c.c. of the solution, which should contain from 1—1.5 grams of tannins, 3 grams of prepared hide-powder is added, and the mixture left for 14—16 hours, being shaken frequently. The liquid is then filtered through paper, and should not give a precipitate either with gelatin solution (1 gram of gelatin, 100 c.c. of water, and 1 c.c. of phenol), or with tannin; a definite portion is then evaporated to dryness, and the weight of the non-tannin solids thus obtained deducted from that of the residue left by the infusion before treatment with hide-powder.

The hide-powder is prepared as follows: The commercial product is treated 8 times with 20 times its bulk of water, thrown on a cloth filter, and well pressed; it is then treated with 10 times its amount of alcohol, again collected and pressed, then dried at 100°, and powdered. It will then be in excellent condition, and contain about 7 per cent. of moisture.

The author has tried the “silk process” recommended by Vignon (this vol., ii, 135), but considers it less satisfactory than the hide-powder method.

L. DE K.

**Testing of Oil and Spirit of Mustard.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 110—111).—The following method is recommended in place of that prescribed by the German Pharmacopœia. Oil of mustard is first converted into spirit of mustard by diluting 2 grams of it with 98 grams of spirit of wine. Of the spirit of mustard, 5 c.c. (= 4.2 grams) are allowed to remain with 25 c.c. of *N*/10 silver nitrate solution and 5 c.c. of ammonia for 24 hours in a well stoppered flask of 50 c.c. capacity, diluted to the mark, and filtered from precipitated silver sulphide; 25 c.c. of the filtrate are mixed with 4 c.c. of nitric acid and a few drops of ferric sulphate solution, and titrated with *N*/10 ammonium thiocyanate solution; of this, 4.1—4.5 c.c. should be required (corresponding to about 1.852—2.000 per cent. of allylthiocarbimide in the spirit, 92.6 to 100 per cent. in the oil).

C. F. B.

**Preparation and Testing of "Spiritus Cochleariæ."** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 239, 105—110).—The method of preparation prescribed by the German Pharmacopœia, namely, to distil the green, crushed scurvy-grass with alcohol and water, is unsuitable. In the first place, the immediate addition of alcohol prevents the due action of the ferment, by means of which the thiocarbimide is probably formed from some glucoside, and, in the second place, the green plant is available only during a very limited season of the year; nor can the artificial oil of scurvy-grass be employed, for it (at least that supplied by Schimmel and Co.) is isobutylthiocarbimide, whereas the natural oil is secondary butylthiocarbimide. A normally prepared spirit contains 0.06—0.07 per cent. of secondary butylthiocarbimide, and may be prepared suitably from the dry plant in the following manner: Dried scurvy-grass (4 parts) and coarsely powdered white mustard (1 part) are allowed to remain with water (40 parts) for 3 hours in a glass retort; spirit of wine (15 parts) is then added, and 20 parts are distilled over. (The dried scurvy-grass does not contain the ferment present in the green plant; the mustard is intended as a substitute for it.) The distillate is a clear, colourless, feebly dextrorotatory liquid with a peculiar odour and penetrating, burning taste; it has a sp. gr. 0.908—0.918.

The purity of the spirit may be tested by heating 50 grams with 5 c.c. ammonia for a few hours on the water-bath in a flask furnished with an air condenser, evaporating to dryness, extracting the residue with a little alcohol, and allowing the filtered alcoholic extract to evaporate on a watch glass; the melting point of the crystals should lie between 125° and 135°. (Pure secondary butylthiocarbamide, 136—137°. The thiocarbamides derived from the probable adulterants are those of allyl, melting at 72—74°; normal butyl, 79°; isobutyl, 93.5°; tertiary butyl, 165°.)

The strength of a pure spirit is ascertained by allowing 50 grams to remain with 10 c.c. *N*/10 silver nitrate solution and 5 c.c. ammonia solution for 24 hours in a well stoppered flask of 100 c.c. capacity, diluting to the mark, filtering from the precipitated silver sulphide, adding to 50 c.c. of the filtrate 4 c.c. of nitric acid and a few drops of ferric sulphate solution, and titrating with *N*/10 ammonium thiocyanate solution; of this, not more than 2.5 c.c. should be used (this corresponds with a minimum of 0.0575 per cent. of secondary butylthiocarbimide in the spirit).

A qualitative and quantitative examination may be combined in one operation by means of the polarimeter, secondary butylthiocarbamide having a specific rotation  $[\alpha]_D = +33.43^\circ$ . Of the spirit, 100 grams are heated with 10 c.c. of ammonia for 3 hours on the water-bath, in a flask furnished with an air condenser, the liquid is evaporated, the residue dissolved in 10 c.c. of warm water, and the solution, filtered if necessary, examined in a 2 dcm. tube in the polarimeter; it should have a rotation of about 0.5° (which corresponds to 0.06515 per cent. of secondary butylthiocarbimide in the original spirit). C. F. B.

**Silicotungstic Acid as a Reagent for Alkaloids.** By GABRIEL BERTRAND (*Compt. rend.*, 1899, 128, 742—745).—Silicotungstic acid

has great advantages as a general reagent for alkaloids; it is extremely sensitive, its molecular weight is very high, and the compounds which it forms with the alkaloids are definite and very stable. A 5 per cent. solution is convenient. The precipitates are white, yellow, or salmon colour, are flocculent, pulverulent, or even crystalline, and are readily collected and filtered. They are but little affected even by somewhat concentrated acids, and when strongly heated leave a residue of silicic and tungstic anhydrides only. They have the composition  $12\text{WO}_3, \text{SiO}_2, 2\text{H}_2\text{O}, 4\text{A} + n\text{H}_2\text{O}$ , where A is the alkaloid. The quantity of water of crystallisation varies with the alkaloid, and part at least is expelled at  $120^\circ$ . The pyridine compound crystallises with  $\text{H}_2\text{O}$ , the morphine compound with  $9\text{H}_2\text{O}$ , and the strychnine compound with  $8\text{H}_2\text{O}$ . If the precipitates are heated in the liquid in which they are formed, they lose water, and in some cases, such as aconitine and veratrine, the character of the precipitate becomes so altered that it is more readily visible and the sensitiveness of the reaction is greatly increased. The limits of the reaction, using 5 c.c. of the alkaloid solution and adding 1 to 2 drops of the reagent and 1 to 2 drops of dilute hydrochloric acid (1:10), are as follows: Conicine, 1:8,000; morphine, 1:16,000; theobromine, 1:18,000; nicotine, 1:20,000; narceine, 1:30,000; codeine, 1:40,000; atropine and caffeine, 1:50,000; cocaine, 1:200,000; aconitine, 1:80,000; veratrine, 1:130,000; brucine, 1:150,000; strychnine and narcotine, 1:200,000; quinine, quinidine, cinchonine and cinchonidine, 1:500,000. In the case of aconitine and the following alkaloids, the sensitiveness of the reaction is increased after adding the reagent by boiling the liquid and then cooling, and the limits specified apply to this manner of working.

Since the silicotungstates are attacked by oxidising agents, the characteristic colour reaction of the alkaloid can often be applied directly to the silicotungstic precipitate. The alkaloids are, however, very easily liberated from the precipitate by treatment with dilute alkali hydroxide solutions; the silicic and tungstic acids dissolve, and the alkaloid either remains insoluble or dissolves, as the case may be.

C. H. B.

**Estimation of Alkaloids in Pomegranate Bark.** By ERICH EWERS (*Arch. Pharm.*, 1899, 237, 49—57).—The following modification of Keller's process for estimating nicotine (*Ber. pharm. Ges.*, 1898, 145) has been found suitable:—Six grams of the powdered bark are placed in a vessel of 200 c.c. capacity, 60 c.c. of ether, 60 c.c. of light petroleum, and 10 c.c. of 20 per cent. aqueous caustic potash or soda are added, and the mixture is shaken long and vigorously at intervals during half an hour, after which it is allowed to remain for four hours. One hundred c.c. of the ethereal solution are poured off through a small filter into a vessel of 200 c.c. capacity, 10 drops of an alcoholic solution of methyl orange are added, and  $N/20$  acid is added, a little at a time, until a slight excess is present; after each addition the mixture is vigorously shaken, a pink colour in the aqueous solution after it has settled indicating excess of acid. This excess is then titrated with  $N/50$  caustic potash, the mixture being

shaken after each addition as before. The number of c.c. of  $N/20$  acid used multiplied by 0.007375 gives the weight of alkaloids contained in 5 grams of the bark. Specimens of the bark of roots coming from S. France contained 0.63—0.72 per cent. of alkaloids, of the bark of branches, 0.52 per cent. The percentage diminishes when the drug is stored; samples purchased in druggists' shops contained from 0.40—0.41 when stored whole or in chips, 0.33—0.38 when stored in the form of powder.

It is said that, of the alkaloids contained in the bark, only the pelletierine and isopelletierine are of value as a vermifuge, the pseudopelletierine and methylpelletierine having but little effect. In order to estimate the former, the mixture left at the close of the titration described above is made just acid with  $N/20$  acid, 2 grams of sodium hydrogen carbonate are added, and the whole is shaken vigorously. (The alkali decomposes the salts of pseudo- and methylpelletierine only.) After the mixture has remained for half an hour, 90 c.c. of the ethereal solution are filtered off, and titrated as above with  $N/20$  acid, the excess of the latter being determined with  $N/50$  alkali. The number of c.c. of acid used is divided by 0.9, and the quotient is subtracted from the number of c.c. used in the titration of the total alkaloids; the remainder multiplied by 0.00705 gives the weight of pelletierine and isopelletierine in the bark. These were found in various samples to form 40—50 per cent. of the total alkaloids present; as the variation is so slight, a determination of the total alkaloids suffices to indicate the value of a sample of the drug.

C. F. B.

**Estimation of Urinary Indican.** By EYVIN WANG (*Zeit. physiol. Chem.*, 1899, 27, 135—140).—Fresh work has shown the necessity of modifying the process previously described (Abstr., 1898, ii, 659), so that it now runs as follows: The urinary indican is precipitated with a 20 per cent. solution of lead acetate. The clear filtrate is treated with an equal volume of Obermayer's reagent, and the indigo extracted with chloroform. The chloroform is distilled off, and the residue, after cooling, washed out with a mixture of equal volumes of ether, alcohol, and water; the particles of indigo are collected on a filter and dried. The dried deposit is thoroughly boiled with chloroform; the chloroform is then distilled off, concentrated sulphuric acid added, and after some hours the solution is diluted with water, filtered, and titrated.

W. D. H.

**Estimation of Indoxylsulphuric (Indican) Acid in Urine.** By FRITZ OBERMAYER (*Chem. Centr.*, 1899, i, 68—69; from *Wien. klin. Rundschau*, 1898, 537).—10 or 20 c.c. of the urine are diluted to 50 c.c. and mixed in a separating funnel with 50 c.c. of fuming hydrochloric acid containing 1—2 grams of ferric chloride per litre. After 15 minutes, the indigo which has been formed from the indican is isolated by first agitating with 25 c.c. and then with repeatedly renewed quantities of 10 c.c. of chloroform. The chloroform extract is evaporated and the residue heated for a few minutes on the water-bath with 50 c.c. of 45 per cent. alcohol to remove other colouring matters, the alcohol being carefully poured off. The indigo, which



adheres firmly to the dish, is then dissolved in 5 c.c. of strong sulphuric acid, gently heated for 15 minutes on the water-bath, the solution, after cooling, diluted to a definite volume, and an aliquot part titrated at 50—80° with a solution of potassium permanganate containing 0.0256 gram per litre, 1 c.c. of which equals 0.0005 gram of indigotin. It is advisable to make a preliminary rough estimation in order to judge how much urine should be used. Some impurities may be removed by the careful addition of a solution of lead acetate (1 : 5) avoiding any excess (Abstr., 1891, ii, 248).

L. DE K.

**Estimation of Bile-pigment in Urine.** By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1899, 27, 83—94).—The method previously described (Abstr., 1894, ii, 466) is well suited for the estimation of bile-pigment in urine.

W. D. H.

**Detection of Urobilin in Urine.** By SAILLET (*Zeit. anal. Chem.*, 1899, 38, 131; from *Rev. méd.*, 1897, No. 2).—Freshly passed urine contains, not urobilin, but its chromogen, which, however, by exposure to sunlight for a few minutes, or to diffused daylight for several hours, is converted into urobilin. From urine acidified with acetic acid, ethylic acetate extracts the urobilinogen, and does not give it up to water, but after exposure to light, or the addition of nitric acid, urobilin can be removed by water and approximately estimated by spectrophotometry.

M. J. S.

**Ammonium Persulphate as a Reagent for the Detection of Albumin in Urine.** By CASIMIR STRYZYROWSKI (*Chem. Centr.*, 1899, i, 151—152; from *Schweiz. Wochschr. Pharm.*, 36, 545—546).—5 to 10 c.c. of the filtered urine is placed in a test-tube and, by means of a pipette, a 10 per cent. solution of ammonium persulphate is introduced below the liquid. If albumin is present, a greyish-white ring forms at the surface of contact of the liquids. The test still shows at a dilution of 1—100,000; it is not interfered with by peptones or urates, but in the presence of biliary matters the ring is coloured green.

L. DE K.

**Detection and Estimation of Proteids, Diastases, Alkaloids, Leucomaines, and Toxins, especially in Urine.** By PAUL CHIBRET (*Compt. rend.*, 1899, 128, 431—433).—A solution of iodine, 47 grams, and potassium iodide, 58 grams, in water, 60 grams, is employed as a reagent for the detection of nitrogenous bases, peptones, proteids, leucomaines, toxins, &c., in water or urine, and their approximate estimation by observing the degree of dilution at which a standard turbidity is produced. The reagent has no action on urea or uric acid.

In a very carefully cleaned tube, 2 c.c. of a solution of 1 part of cocaine hydrochloride in 800,000 parts of water is mixed with 3 drops of nitric acid and 3 drops of the iodine reagent, and the liquid seems to remain clear, but if very carefully observed under suitable conditions of lighting is found to be slightly opalescent; this is the standard of turbidity. It does not represent the limit of the reaction, which is 1 : 2,000,000, but is a convenient standard to work with. The degree of dilution necessary to give the same turbidity is, with egg albumin

and peptones, 1 : 20,000; creatinine, 1 : 1000; xanthine, 1 : 5000; pepsin, 1 : 50,000, and alkaloids, 1 : 800,000. In the case of proteids in urine, if they are of alimentary origin the necessary dilution is from 1 : 20,000 to 1 : 50,000, but if they are pathological products they may require dilutions of 1 : 140,000 or even 1 : 400,000.

Normal urine gives the turbidity with a dilution of 1 : 30 to 1 : 40, but with malnutrition this may rise to 1 : 10. In the case of febrile and infectious diseases, the dilution may be 1 : 100 or even 1 : 200. The difference between the necessary coefficient of dilution before and after precipitation of the albumin gives the coefficient due to the albumin.

C. H. B.

**Artificial Digestion of Food Constituents.** By KONRAD WEDEMEYER (*Landw. Versuchs-Stat.*, 1899, 51, 375—385).—To avoid uncertain results, gastric juice must be prepared from a large number of stomachs, and the amount of liquid obtained being more than is required for immediate use, it was proposed (Stutzer, *Abstr.*, 1890, 275) to add salicylic acid in order to prevent its decomposition. Stutzer subsequently found thymol to be more suitable (*Landw. Versuchs-Stat.*, 1892, 40, 163).

Experiments are now described in which thymol (0.1), chloroform (0.5), formaldehyde (0.2), and toluene (0.5 and 1.0 per cent.) were employed for preventing the decomposition of the juice. This retains its activity for a considerable time when none of these substances are added, but soon acquires an intolerable odour. Chloroform was found to be the most suitable substance in digestion experiments with cotton-seed meal; with thymol, less of the nitrogen was digested. With other foods, the various substances behaved somewhat differently; formaldehyde, for instance, diminished the digestibility of brewers' grains, but not that of wheat bran. Further experiments showed that a solution of pepsin is more suitable, as well as much more convenient, than gastric juice. The process is as follows: The food (2 grams) is mixed in a beaker with 490 c.c. of water containing 1 gram of pepsin and 10 c.c. of 25 per cent. hydrochloric acid, and digested for 48 hours at 37—40°, being frequently stirred. After 24 hours, another 10 c.c. of the same acid is added. Finally, the whole is filtered, the undissolved substance washed successively with hot water, alcohol, and ether, and the nitrogen determined (in both substance and filter). The results differed at most from those obtained with gastric juice by +0.079 and -0.096 per cent., being in 17 cases somewhat higher, and in 11 cases somewhat lower.

N. H. J. M.

## General and Physical Chemistry.

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**A Source of Intense Monochromatic Light.** By CH. FABRY and A. PEROT (*Compt. rend.*, 1899, 128, 1156—1158).—An electric arc is employed passing between mercury poles in a vacuum. The apparatus consists of a cylindrical glass bulb filled to one-third its height with mercury, which is divided into two masses insulated from one another by means of a glass tube concentric with the walls of the bulb and opening nearly on a level with the mercury. Each mass of mercury is connected with a pole of a source of a continuous current by means of platinum wires fused through the glass. The bulb is made as completely vacuum as possible, and in order to strike the arc the apparatus is slightly shaken, which brings the two masses of mercury momentarily in contact. The difference of potential between the poles does not exceed 15 volts, but in order to secure a steady arc, 30 volts should be available. A current of two to three ampères is sufficient, but stronger currents may be used, and the intensity of the light may reach 1 Carcel (approx. 7·4 candles).

The spectrum of the light is identical with that of the light from Michelson's mercury vapour tubes, and consists of a violet ray 4358·0, a green ray 5460·7424, and two yellow rays 5769·5984 and 5790·6593; the separate rays can be isolated by means of a prism or by the use of suitable absorbents, such as yellow glass or potassium dichromate for the violet ray, a saturated solution of didymium chloride for the two yellow rays, and a solution of eosin for the violet and green rays. For photographic purposes, the ultraviolet rays should be cut off by an acid solution of quinine sulphate.

C. H. B.

**Double-trough Refractometer, and Experiments therewith on Solutions of Cadmium Bromide, Sugar, and Di- and Trichloroacetic Acids and their Potassium Salts.** By WILHELM HALLWACHS (*Ann. Phys. Chem.*, 1899, [ii], 68, 1—45).—A form of refractometer is described which consists essentially of a trough of which two opposite sides are formed by two slightly inclined plates of glass with parallel surfaces. This is divided into two by a partition of glass with sides not perfectly parallel. On one side of the partition the trough contains water, and on the other the liquid under examination (*Ann. Phys. Chem.*, 1893, [ii], 50, 577). The incident ray grazes the surface of the partition, passes into it at the critical angle, enters the second liquid, and finally emerges from the trough. The angle between the emergent rays when the incident ray is (1) direct, (2) reversed, is observed, and from this the difference between the refractive indices of the two liquids. The necessary calculations are given and the required expressions deduced, and experiments are recorded to show the accuracy attainable as well as the effect of temperature changes in either or both the trough divisions; differences of 0·0003 in the indices of refraction appear to be measurable with an accuracy of about 0·0000015. Le Blanc and Rohland

(Abstr., 1896, ii, 345) have found that the difference between the molecular refraction of cadmium bromide and iodide, which are but slightly dissociated, varies considerably from that between other more highly dissociated bromides and iodides in solution, but the author's results are not in accord with these, whilst he also shows that the density observations of Le Blanc and Rohland for cadmium bromide do not agree with those of Grotian and Kremers. The error was probably due to the neglect of the hydration of cadmium bromide, as corrections on this assumption bring all the observations into accord, and no indication is given of dependence of refraction on dissociation. For solutions of cane sugar, the change in the refraction is only about 0.4 per cent. between 0.4 and 13 per cent. solutions. A comparison of the differences between the refraction of the acid and its potassium salt in the cases of hydrochloric, dichloroacetic, and trichloroacetic acids shows that at great dilution the differences are very nearly equal—4.6 to 4.9—whereas at higher concentrations the differences are considerably greater, so that in hydrogen salts a connection between refraction and dissociation is indicated, as stated by Le Blanc (*loc. cit.*).  
L. M. J.

**Internal Resistance of Normal Cells.** By ERNST COHEN (*Zeit. physikal. Chem.*, 1899, 28, 723—736).—Measurements of the internal resistance of Clark's and Weston's cells have yielded very diverse values, and the author has investigated the cause of these differences. It was found that the formation of crystals between the electrodes greatly increases the resistance of saturated solutions of zinc sulphate, whilst the resistance is also dependent on the arrangement of the crystals, and this is the cause of the various values found with the normal cells. When filled with a clear saturated solution, the resistance of a Clark's cell at different temperatures was found to be proportional to that of the zinc sulphate solution, and analogous results were obtained with Weston cells. Thus prepared with clear solutions and a small quantity of depolariser, normal cells can be conveniently employed for the graduation of galvanometer readings. L. M. J.

**Relation between the Dissociative Power, the Dielectric Constant, and the Molecular Condition of Liquids.** By HANS EULER (*Zeit. physikal. Chem.*, 1899, 28, 619—628).—According to Dutoit, Aston, and Friderich, the dissociative power of a solvent is a direct function of its molecular association (Abstr., 1897, ii, 546); Nernst has also shown that a probable connection exists between the dissociative power and the dielectric constant (Abstr., 1894, ii, 266). As, however, the associated solvents employed by Aston and Dutoit in all cases had a high dielectric constant, further investigation was necessary. Solutions of potassium iodide and chloride, and of sodium bromide and iodide in nitrobenzene, benzonitrile, and furfuran, were found to have considerable conductivity, and are hence dissociated, although the solvents are in each case non-associated or monomolecular. In the case of the solutions in benzonitrile, the molecular conductivity was found to increase with the concentration, and this is considered to be due to an increased dissociative power owing to the presence of ions; this explanation probably accounts also for some of the exceptions

from the dilution law. The molecular conductivity of the same salts in butyric, isobutyric, and valeric acids was found to be exceedingly small, although the association of the solvents is great. The dielectric constants are, however, also small, and Nernst's hypothesis is hence supported. L. M. J.

**Electric Conductivity of Salt Solutions.** By R. GOLDSCHMIDT and ALBERT REYCHLER (*Bull. Soc. Chim.*, 1898, 19, [iii], 675—684).—An apparatus is described for determining electric conductivity, which is much smaller than the forms employed by Kohlrausch and Arrhenius. The electrolytic cell consists of a small ebonite cup, at the bottom of which is placed a platinum electrode coated with platinum black; the second electrode is fixed to the lower end of a vertical ebonite rod, and both the rod and the cup can be moved to and from each other in a vertical direction by means of micrometer screws. The exact distance between the electrodes is ascertained by means of a vernier and graduated circle attached to the movable parts of the apparatus. In one series of experiments, the diameters of the cup and electrodes were 47 mm. and 40 mm. respectively; a  $N/50$  solution of potassium chloride was employed as the electrolyte, and the temperature of the apparatus was maintained at  $18^\circ$ . The electric capacity of the apparatus was calculated from the equation,  $0.002244 = 1/R \times \text{capacity}$ , the fraction 0.002244 being Kohlrausch's value for the specific conductivity of the solution, the value of the resistance,  $R$ , being determined with the electrodes at varying distances apart. These values were employed in determining the specific conductivity of a  $N/500$  solution of the same electrolyte. The results are arranged in tabular form and compared with those obtained from an apparatus of the Arrhenius form.

A second series of experiments was made with a smaller apparatus, the diameters of the cup and electrodes in this case being 17.3 mm. and 14.3 mm. respectively, and the cup having a capacity of 3 c.c. It is found that the conductivity increases as the distance between the electrodes diminishes. The irregularity observed when the electrodes are very close together is due, not only to polarisation, but also to the abnormal behaviour of the layers of the solution in close proximity to the electrodes. The ratio between the increase of resistance and the increase of the distance between the electrodes is constant only for that portion of the electrolytic solution where the equipotential surfaces are plane and parallel to each other; this condition does not obtain in the immediate neighbourhood of the electrodes. In order to eliminate this source of error, the conductivity of the solution is calculated in the following manner:  $R_m$  and  $R_n$  being the resistances obtained with the standard solution when the electrodes are  $m$  and  $n$  millimetres apart, and  $R'm$  and  $R'n$  the corresponding values for the solution under investigation, the specific conductivity of the latter is  $0.002244 \times (R_m - R_n)/R'm - R'n$ . A table is given which shows that, by the aid of this expression, it is possible to obtain accurate results with the smaller apparatus; in working with this form, it is convenient to fix the key of the Kohlrausch bridge at a convenient resistance, and then to make the final adjustment by

means of the micrometer screw of the upper electrode. The electric capacity of the instrument having been previously determined for any position of the electrodes, the specific conductivity is readily obtained from the equation  $\text{sp. c.} = 1/R' \times \text{capacity}$ . G. T. M.

**Electrical Oscillations.** By HUGO KAUFFMANN (*Zeit. physikal. Chem.*, 1899, 28, 673—707).—Drude has shown that hydroxy-compounds are characterised by anomalous absorption of electrical oscillations (*Abstr.*, 1897, ii, 537). The author, however, shows that this is not limited to such compounds, and considers it to be associated with compounds containing some feeble union. In the series of saturated fatty alcohols, the extent of this absorption does not follow the same order as the velocities of hydrolysis, which may be taken as a measure of the looseness of the hydrogen union in the hydroxyl, and the author therefore considers that the absorption is most marked for a certain "critical stability" and decreases as the stability is removed in either sense from this. Besides hydroxyl, the following groups appear to cause anomalous absorption: nitro-group,  $\text{NO}_2$ ; azoxy-group,  $\text{N}_2\text{O}$ ; the characteristic group,  $:\text{CH}$ , in the leuco-bases, and the carboxyl group in the ethereal salts of substituted carboxylic acids. The absorption of Tesla oscillations by organic compounds in the state of vapour was also further examined (*Abstr.*, 1898, ii, 550), about 75 more compounds being investigated. The following generalisations are now deducible. Aromatic compounds exhibit a much more marked luminescence than aliphatic compounds. Halogens or the nitro-group destroy or weaken the luminescence (this is very marked in naphthalene compounds). Introduction of an acetyl group in a hydroxy-compound or an amine destroys or lowers the luminescence, but the introduction of an alkyl group has no effect. The amido-group converts an inactive into an active compound, whilst two hydroxyl groups produce the same effect, one being, however, insufficient; the author applies the term 'auxochrome' to the groups  $\text{NH}_2$  and  $\text{OH}$  or their derivatives. In di-derivatives of the benzene series, the para-compound is, as a rule, the most active, the cause of the activity probably lies in the nature of the benzene nucleus, and in active compounds there appears to be a predisposition to the formation of compounds of quinonoid structure, although the quinones themselves are inactive. L. M. J.

**Regularities in the Boiling Point of Liquids in Exhausted Vessels.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1623—1635 Compare *Abstr.*, 1896, ii, 89, 464 and 635).—I. In the distillation of high molecular liquids in the vacuum of the cathode light, the difference in temperature between the liquid and vapour is very slight; thus, palmitic acid, boiling in the vacuum of the cathode rays, showed a temperature of  $137.5$ — $138^\circ$  in the liquid, and  $136$ — $137^\circ$  in the vapour. The boiling point is, however, influenced very largely by the height of the vapour column above the liquid; thus, elaidic acid begins to boil at  $142^\circ$ , but the boiling point rises to  $154^\circ$  as the vapour column mounts up to the side-limb of the distilling flask, 65 mm. above the surface of the liquid. The vapour column is very sharply defined; it

can be measured to 1 mm., and a bright cathode light can be obtained only 20 or 30 mm. above the limit of the saturated vapour.

II. By exact measurement, it was found that phenyl pentadecyl ketone boiled at  $161^{\circ}$  under a vapour column of 90 mm., at  $164.5^{\circ}$  for 110 mm., at  $170.5^{\circ}$  for 145 mm., and at  $176^{\circ}$  for 180 mm., giving an average rise of  $1.66^{\circ}$  in the boiling point for an increase of 10 mm. in the height of the vapour column. An increase in the height of the vapour column from 65 to 180 mm. gave, for lauric acid, mol. wt. 200, a rise in boiling point of  $9.5^{\circ}$ ; for palmitic acid, mol. wt. 256, a rise of  $15.7^{\circ}$ , and for elaidic acid, mol. wt. 282, a rise of  $19^{\circ}$ ; these increments are not proportional to the molecular weights, but the value for palmitic acid is  $6.2^{\circ} = 2 \times 3.1^{\circ}$  greater than that for lauric acid for a difference of 56 in mol. wt., whilst the value for elaidic acid is  $9.5^{\circ} = 3 \times 3.16^{\circ}$  greater for a difference of 82 in mol. wt. The rise of temperature on increasing the height of the vapour column from 65 to 175 mm. was  $18^{\circ}$  for hexadecane, mol. wt. 226, and  $36^{\circ}$  for dotriacontane, mol. wt. 450, so that an exact proportionality appears to exist in the paraffin series.

III. The interval between the melting point and the boiling point of the higher paraffins under 15 mm. pressure increases by  $6^{\circ}$  for each additional  $\text{CH}_2$  group. If, however, the boiling points are determined in a vacuum at 0 mm. pressure, with a vapour column of 65 mm., the regularity is still more marked, for the interval between melting point and boiling point can be calculated directly from the formula  $n \times 4.22^{\circ}$ , where  $n$  is the number of carbon atoms in the molecule; the agreement between the observed and calculated values is very close from  $\text{C}_{20}\text{H}_{42}$  to  $\text{C}_{32}\text{H}_{66}$ , but for the lower homologues the calculated values are always greater than the observed, the deviation being explained by the gradual change in the percentage composition of the paraffin. For the fatty acids, the corresponding increment is about  $4.6^{\circ}$  for each additional  $\text{CH}_2$  group. T. M. L.

[Thermochemistry of] Morphine and its Salts. By ÉMILE LEROY (*Compt. rend.*, 1899, 128, 1107—1110).—The heat of combustion of hydrated morphine is 2146.7 Cal. at constant pressure and 2145.2 Cal. at constant volume. The heat of solution of the anhydrous base is 8.51 Cal., and that of the hydrate is 4.85 Cal.; hence the heats of hydration of morphine with water and ice are 3.66 and 2.10 Cal. respectively. The heat of formation of anhydrous morphine from its elements is 108.24 Cal. The following table gives the heat of neutralisation with various acids.

	Morphine hydrate.	Anhydrous base.
Hydrochloric acid.....	3.52 Cal.	7.18 Cal.
Sulphuric     " ( $\frac{1}{2}\text{H}_2\text{SO}_4$ )...	4.85   "	8.51   "
Nitric         " .....	3.39   "	7.05   "
Acetic         " .....	2.70   "	6.36   "
Oxalic         " ( $\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4$ )..	3.66   "	7.32   "

The addition of excess of acid produces a slight thermic effect, which is positive in the case of the monobasic acids and negative with the dibasic acids; the addition of excess of base is not accompanied by any thermal change.

The heats of solution of the crystalline salts,  $\bar{M}, HCl, 3H_2O$ ,  $M_2, H_2SO_4, 5H_2O$ , and  $M_2, H_2C_2O_4, 4H_2O$ , are  $-9.47$ ,  $-9.74$ , and  $-9.87$  Cal. respectively; the heat of hydration of the hydrochloride with  $3H_2O$  (liquid) is  $6.08$  Cal., and with  $3H_2O$  (solid)  $1.39$  Cal. The heat of formation of the dry hydrochloride from anhydrous morphine and hydrogen chloride is  $27.97$  Cal.; the corresponding constants for isoquinoline and paratoluidine are  $25.67$  and  $23.65$  Cal. respectively; morphine is the stronger base; it is alkaline to litmus, whereas the other two are not. The heat of solution of morphine hydrate in dilute caustic potash at  $12^\circ$  is  $4.79$  Cal.; the heat of formation of the potassium derivative from anhydrous morphine is  $8.45$  Cal., whereas that of potassium phenoxide from solid phenol and dilute potash solution is only  $5.6$  Cal. The addition of a second molecule of morphine or alkali hydroxide produces a development of heat; this result indicates that the potassium derivative is slightly dissociated in aqueous solution. The heat developed by the decomposition of morphine hydrochloride (1 mol.) dissolved in 10 litres of water by caustic potash (1 mol.) is  $10.52$  Cal.; when the precipitated morphine is redissolved by the addition of more potash (1 mol.), the heat generated is  $4.75$  Cal.; this value is almost identical with the heat of solution of crystallised morphine hydrate in caustic potash. The heat effect due to the precipitation of the alkaloid is not produced instantaneously, but during an interval of 2 or 3 minutes; these results indicate that morphine liberated from its salts by an alkali is slowly converted into the hydrated form.

G. T. M.

**Increase of Pressure caused by the Mixture of two Gases, and the Compressibility of the Mixture.** By DANIEL BERTHELOT (*Compt. rend.*, 1899, 128, 1159—1160).—The values calculated for the increase in pressure due to the mixing of gases, assuming a series of operations such that diffusion takes place in a state of perfect gas and using the values for compressibility determined by the author and Sacerdote (this vol., ii, 404), agree closely with the experimental results, and hence the use of the cycle proposed (*loc. cit.*) is justifiable. C. H. B.

**Calculation of the Compressibility of a Gaseous Mixture from that of its Components.** By DANIEL BERTHELOT (*Compt. rend.*, 1899, 128, 1229—1231).—A mathematical discussion not suitable for abstraction.

G. T. M.

**Baumé's Hydrometer—American Standard.** By SIDNEY S. EMERY (*J. Amer. Chem. Soc.*, 1899, 21, 119—132).—Tables are given of the specific gravities corresponding with every  $1/10$  or every  $1/8$  degree of Baumé's scale, from sp. gr.  $0.6667$  to  $1.9833$ . T. M. L.

**Specific Gravity of some Liquefied Gases.** By ALBERT LADENBURG and C. KRÜGEL (*Ber.*, 1899, 32, 1415—1418).—Having been made acquainted with Dewar's researches on the subject (*Proc. Roy. Inst.*, 1896, 15, 138; compare *Proc.*, 1895, 11, 226), the authors have re-



determined the specific gravity of certain liquefied gases by weighing in the liquid a sinker, not of glass (compare this vol., ii, 208) but of silver (Dewar, *loc. cit.*); the results are now found to be more in harmony with his. Liquid oxygen has the density 1.134 (Dewar 1.1375); liquid ethylene, 0.6095; whilst a liquefied mixture of oxygen and nitrogen containing  $x$  per cent. of oxygen has the density  $d = 0.86 + 0.00289x$  (experimental numbers:  $d = 1.015, 1.068, 1.133$  when  $x = 53.6, 72.15, 94.4$  respectively).

By weighing sinkers of silver, ordinary glass, Jena glass and silver in succession in liquid air, and assuming the coefficient of expansion for silver given above, the mean coefficient of expansion between the ordinary temperature and that of liquid air (density 1.1215) boiling under atmospheric pressure was found to be 0.00003104 for ordinary glass, 0.00001822 for Jena glass.

C. F. B.

**New Apparatus for the Determination of Volume.** By CHARLES F. MCKENNA (*J. Amer. Chem. Soc.*, 1899, 21, 50—52).—An improved form of volumenometer of the Schumann or Candlot type. It consists of a flask of about 175 c.c. capacity with two vertical necks, one of which, having a diameter of about 5 mm., is graduated in tenths of a c.c., and closed at the top by a perforated stopper. The other tube, which is shorter, has a zero mark at about its middle point, on either side of which it is graduated for one or two c.c.; above the graduation, it expands to about 25 mm. diameter, and into it fits a perforated glass stopper, connected by means of a tube fitted with a stopcock with a rubber bulb. The mode of using is as follows. Liquid is introduced into the flask, the level in the shorter tube adjusted to zero by means of the rubber bulb, and the volume obtained by reading off the position of the liquid in the other limb. After removing the stopper from the shorter tube, the powdered solid is sifted in, the liquid adjusted to zero, and the volume again read off on the longer tube. The apparatus can be conveniently used with about 10 grams of material.

T. H. P.

**Composition of Mixed Vapours.** By HECTOR R. CARVETH (*J. Physical Chem.*, 1899, 3, 193—213).—In only a few exceptional cases does the vapour given off by a binary system possess the same composition as the liquid, and although of great importance in fractional distillation, the connection between the composition of the two phases has been little studied. A form of apparatus for the determination of the composition of the vapour is described, the principle of the method being that the condensed vapour is returned to a small receiver within the larger flask containing the solution whose boiling point is being taken, and in this receiver is made to boil. From this boiling point, the composition of the condensed vapour is determined by comparison with the boiling point curve of the two liquids. The cases examined were mixtures of (1) acetone and water, (2) benzene and carbon bisulphide, and the temperature | composition curves for liquid and vapour are given. The results obtained are verified by comparison with those derived from the direct analysis of the liquid volatilised between two temperatures sufficiently near to allow of a mean being taken. Brown's method of a constant temperature still-head

(Trans., 1881, 39, 304) is inaccurate, as discrepancies are found in his results, the composition of the vapour being always displaced to the side of the more volatile compound. Purity of a compound is in general indicated by the identity of the boiling points of the liquid and condensed vapour. During the experiments, it was noticed that, in many cases where the composition of liquid and condensed vapour differ considerably, the Beckmann apparatus does not yield accurate results, differences of one degree being obtained by alteration of the rate of boiling.

L. M. J.

**Molecular Weights of Liquids. III.** By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1899, 21, 282—287. Compare this vol., ii, 145).—From Leffeldt's vapour-pressure measurements (this vol., ii, 11), it is concluded that, in mixtures of benzene and toluene with carbon tetrachloride, both constituents have a normal molecular weight. When mixed with alcohol, however, both benzene and toluene are said to be highly polymerised, especially when the proportion of alcohol is small; the alcohol is regarded as highly polymerised in presence of a small proportion of toluene, but less so when the proportion is large; in benzene solution, the alcohol is regarded as being highly polymerised at all concentrations.

T. M. L.

**Continuous Change from Solid to Liquid.** By GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1899, 28, 629—672).—It having been suggested that crystalline-liquids are in a state approximating to the critical state (this vol., ii, 360), experiments were made to determine whether the heat of transition of the compounds becomes zero at higher pressures. The value of the heat of transition (that is, the change from crystalline-liquid to isotropic) is calculated from the lowering of the transition temperature by means of the expression  $L = 0.02n \cdot T^2/d$ , where  $d$  is the depression produced by  $n$  gram-molecules dissolved in 100 grams of the solvent, and  $T$  the absolute transition temperature. The temperatures were determined at pressures up to 300 atmospheres in the case of parazoxyanisole and parazoxyphenetole, and of solutions of thymol in these solvents. The latent heats of transition for parazoxyanisole thus found were  $L_0 = 4.33$  and  $L_{300} = 4.36$  cal.; and for parazoxyphenetole  $L_0 = 7.2$  and  $L_{300} = 6.6$  cal., so that the experimental pressures appear to be far removed from the critical pressure. The latent heat is also calculable from the volume change and the pressure coefficient of the temperature, but the values so calculated do not agree with the previous results, being far smaller. The cause of this difference is probably the solubility of the thymol in the crystalline-liquid, as not only the transition temperature, but also the melting point, is lowered by the addition of the thymol. The existence of a critical point for the solid crystalline-liquid was also investigated by the determination of the lowering of the melting point at various pressures, and application of the van't Hoff formula. The values so obtained were: parazoxyanisole,  $l_0 = 29$  cal.,  $l_{300} = 36.5$  cal.; parazoxyphenetole,  $l_0 = 14.7$ ,  $l_{300} = 22.3$  cal., so that the critical pressure appears to be a negative pressure of about 1000 atmospheres. For both compounds, the temperature range of the crystalline-liquid increases with

rise of pressure, so that a negative pressure is also indicated for the disappearance of this state. The pressure coefficients of the melting and transition points were also determined for pure cholesteryl benzoate, and from these, and the volume change, the heat of transition is calculated as 0.32 cal. The latent heat of fusion was also similarly determined for paratoluidine, benzene, and camphor, and in each case it was found to decrease with rise of pressure, the values obtained being: paratoluidine,  $l_0 = 39$ ,  $l_{300} = 37.1$ ; benzene,  $l_0 = 30.2$ ,  $l_{300} = 27.7$ ; camphor,  $l_0 = 9.4$ ,  $l_{300} = 8.0$  cal. From these, by subtraction of the external work, the internal heat of fusion is obtained, the difference being about 1 cal. in each case. The effect of pressure on the melting point was also investigated for many organic compounds, the temperature being found in all cases to be a linear function of the pressure, and the following values of the pressure coefficient in degrees per atmosphere were obtained: phenol, 0.0149; thymol, 0.0184; naphthalene, 0.0373; naphthylamine, 0.0200; benzophenone, 0.0289; stearic acid, 0.0258; crotonic acid, 0.0373; orthonitrophenol, 0.0240; phosphorus, 0.0290; menthol (m. p.  $36.5^\circ$ ), 0.0248; menthol (m. p.  $42.5^\circ$ ), 0.0245; monochloroacetic acid, 0.0147. The results for benzene, benzophenone, and phosphorus are shown to be in good accord with observations of Tammann, but the pressures were not carried sufficiently high to indicate curvature of the temperature | pressure curve.

L. M. J.

NOTE.—The results do not appear to agree with those of Damien (*Compt. rend.*, 1891, 112—785), who found in all cases a quadratic formula for the pressure effect. The difference is very marked for naphthylamine, for which Damien found a maximum melting point of  $50.5$  at 81 atmospheres, the value then decreasing to  $49.6$  at 173 atms., whereas the author obtains a steady rise from  $49^\circ$  to  $54.8^\circ$  at 300 atms., the value at 175 atms. being  $52.3$ .

L. M. J.

**Surface-tensions of Solutions of Alkali Chlorides.** By CHARLES E. LINEBARGER (*J. Amer. Chem. Soc.*, 1899, 21, 411—415).—The author has determined the relation between the surface-tensions and concentrations of solutions of lithium, sodium, and potassium chlorides. On constructing curves with surface-tensions as ordinates, and concentrations as abscissæ, it is seen that the curve for sodium chloride lies about midway between those for the potassium and lithium salts, the surface-tension being greater the smaller the molecular weight. If the concentrations be expressed in molecules per litre, the three curves become coincident. The surface-tension is not, as is generally supposed, a linear function of the concentration, as the curves show a slight convexity towards the axis of concentrations.

T. H. P.

**Ternary Mixtures.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 217—231).—It has been shown by Taylor (*Abstr.*, 1897, i, 402), that in a ternary mixture of two non-miscible liquids with a third consolute liquid, the concentrations are connected by the relation  $(C_a A_a)^n = k C_b B_b$  where  $C_a$  and  $C_b$  are the concentrations of the consolute liquid, and  $A_a$  and  $B_b$  those of the other two liquids in

the two phases. Many cases of metallic ternary mixtures have been described by Wright (Abstr., 1891, 1158; 1893, ii, 15, 415, 522; 1894, ii, 419), and the author has examined the results in order to test their agreement with the above expression. The experimental errors were acknowledged by Wright to be great, but notwithstanding this, in some of the systems very fair constancy for  $k$  is obtained. In most cases, except where silver is the consolute metal, the distribution ratio is less than 2, and there appears to be no connection between the distribution ratio at great dilution and the reacting weights of the two metals. Thus in lead-zinc mixtures the ratio varies from 1.5 for tin as consolute to 39 for silver. The inexactitude of the experiments, however, makes further investigation desirable. L. M. J.

**Inversion of Sugar by Salts.** By LOUIS KAHLENBERG, D. J. DAVIS, and R. E. FOWLER (*J. Amer. Chem. Soc.*, 1899, 21, 1—23).—By determining the rate of inversion of sugar by the action of a number of colourless salts, firstly, from the polariscopic readings, and secondly, by calculating the number of molecules in the solution by means of the freezing point method, the authors show that the latter method gives reliable results. By this means, the rates of inversion have been measured for coloured salts with which accurate polariscopic determinations cannot be made. The results show that on arranging the metals according to the speed with which their analogous salts invert sugar solutions, the order is similar to that in the electrochemical series. To this general rule an exception is found in aluminium, the salts of which have relatively a very high velocity of hydrolysis; this may be due to the formation of a colloidal aluminium hydroxide, which would tend to aid the ionic dissociation of the salts and hence promote inversion of the sugar. Confirmation is given of Long's statement (Abstr., 1896, ii, 414, and 1897, ii, 547), to the effect that metallic chlorides invert sugar much more rapidly than the corresponding sulphates, owing to the ionising tendency of chlorine being greater than that of the  $\text{SO}_4$  complex. T. H. P.

**Nature of Valence.** By FRANCIS PRESTON VENABLE (*J. Amer. Chem. Soc.*, 1899, 21, 192—200 and 220—231).—The variation in the valency of an element is explained as due to the necessity for harmony between the motions of the combining atoms, which may be affected by temperature, light or electricity, or by the mutual influence of the atoms. T. M. L.

**The Boiling of Aqueous Colloidal Solutions.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1584—1596).—The salts of the higher fatty acids behave as colloids in aqueous solution, but as crystalloids when dissolved in perfectly dry alcohol. In determining the boiling point of colloidal solutions, a difficulty occurs owing to the formation of bubbles, the tension of which materially increases the pressure on the boiling liquid; this can be largely overcome by using a deep layer of glass beads to break up the bubbles.

The addition of 7.88 grams of sodium palmitate to 30 grams of water raised the boiling point by only  $0.083^\circ$ , whilst if the molecule were dissociated in the ordinary way, a rise of more than ten times this

amount might be expected ; a further addition of sodium chloride gave, however, a normal rise of temperature corresponding with  $M = 26.2$ , the value in pure water being 29.2. With sodium erucate there was a rise of  $0.017^\circ$  (partly due to 1 mm. increase of pressure) instead of  $0.200^\circ$  ; a further addition of sodium chloride gave a rise corresponding to  $M = 27$  instead of 29.2 ; in a second experiment, the rise of temperature was only  $0.001^\circ$  instead of  $0.295^\circ$ , and a subsequent addition of potassium bromide gave  $M = 68$  instead of 59.5. Sodium oleate caused no rise in temperature, although a rise of  $0.58^\circ$  should have occurred if the salt were dissociated in the ordinary way ; subsequent addition of sodium chloride gave  $M = 30.8$  instead of 29.2. Potassium oleate gave a rise of  $0.005^\circ$  instead of  $0.328^\circ$  ; potassium erucate showed a fall of  $0.015^\circ$ , owing to a fall of 0.8 mm. pressure ; potassium stearate gave a rise of  $0.015^\circ$  on adding 3.89 to 30 c.c. of water.

The values of  $M$ , when determined in anhydrous alcohol, were potassium formate, 87.60, theory 84.16 ; potassium acetate, 93.3, 94.9, 96.7, theory 98.18 ; sodium heptoate, 180, theory 152.2 ; potassium heptoate, 153.7, 156.5, 156.5, theory 168.3 ; sodium laurate, 237.2, theory 222.3 ; sodium myristate, 253, theory 250.3 ; sodium palmitate, 282.6, theory 278.4 ; sodium oleate, 301.3, theory 304.4. The presence of a small amount of water in the alcohol causes a very large increase in the values of  $M$ .

T. M. L.

**Crystallisation of Colloidal Salt Solutions.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1596—1608. Compare *Abstr.*, 1896, ii, 468).

—I. The temperature at which aqueous soap solutions gelatinise or deposit a solid soap is determined almost entirely by the melting point of the fatty acid contained in the soap. Thus dry sodium stearate melts at about  $260^\circ$ , but a 20 per cent. solution solidifies at  $69^\circ$ , a 15 per cent. solution at  $68^\circ$ , a 10 per cent. solution at  $68-67^\circ$ , and a 1 per cent. solution at  $60^\circ$ , the melting point of stearic acid being  $69.4^\circ$ . Dry sodium palmitate melts at  $270^\circ$ , but a 20 per cent. solution solidifies at  $62-61.8^\circ$ , and a 1 per cent. solution at  $45^\circ$ , the melting point of palmitic acid being  $62^\circ$ . Dry sodium myristate melts at  $250^\circ$ , but a 20 per cent. solution solidifies at  $53-52^\circ$ , and a 1 per cent. solution at  $31.5^\circ$ , the melting point of myristic acid being  $53.8^\circ$ . Dry sodium laurate melts at  $255-260^\circ$ , but a 25 per cent. solution solidifies at  $45-42^\circ$ , a 20 per cent. solution at about  $36^\circ$ , and a 1 per cent. solution at about  $11^\circ$ , the melting point of lauric acid being  $43.6^\circ$ . The agreement between the melting point of the fatty acid and the temperature at which the sodium salt solidifies from the solution is most marked among the highest homologues, and it is here also that the concentration has least influence on the temperature of solidification.

Similar results are found in the unsaturated series. Dry sodium oleate melts at  $232-235^\circ$ , but a 25 per cent. solution solidifies at  $13-6^\circ$ , the melting point of oleic acid being  $14^\circ$ . Dry sodium elaidate melts at  $225-227^\circ$ , but a 20 per cent. solution solidifies at  $45.5-44.8^\circ$ , the melting point of elaidic acid being  $45^\circ$ . Dry sodium erucate melts at  $230-235^\circ$ , but a 20 per cent. solution solidifies at  $35-34^\circ$ , and a 1 per cent. solution at  $27^\circ$ , the melting point of erucic acid being  $34^\circ$ .

Dry sodium brassidate melts at  $245-248^{\circ}$ , but a 20 per cent. solution solidifies at  $56^{\circ}$ , the melting point of brassidic acid being  $60^{\circ}$ .

In explanation of these observations, it is suggested that when it is dissolved in water, the soap is completely hydrolysed into caustic soda and a fatty acid. The fatty acid is not soluble by itself, but is held in solution by the caustic soda, and the molecules of the fatty acid and base are regarded as grouped into large molecular complexes, giving rise to *colloidal* solutions, as has been shown in the preceding abstract. These colloidal solutions can only exist above the melting point of the fatty acid, but in the lower homologues the melting point is lowered by partial miscibility with water and the soap solution solidifies at a lower temperature, especially when dilute. Crystallisation occurs least readily when the alkali of the soap has a great affinity for water. Thus potassium soaps remain gelatinous at a much lower temperature than sodium soaps; on the other hand, lithium soaps are almost insoluble owing to the feeble affinity of the base for water.

An attempt is made to extend these observations to the hydrochlorides of feeble bases. It is shown that hexadecylamine hydrochloride, which decomposes at  $150^{\circ}$  when dry, crystallises from a 20 per cent. aqueous solution at  $45-42^{\circ}$ , the free base melting at  $46^{\circ}$ . A number of other cases are given, but there does not appear to be any marked relationship between the melting point of the base and the temperature at which the salt solutions crystallise, the discrepancy being perhaps due to the solubility of the amine.

II. 'The crystallisation of salts results from a disturbance of the system present in the solution; the effects of this disturbance are less marked the lower the temperature at which the crystallisation takes place.' Colloidal solutions deposit globular aggregates, and the author has therefore assumed (*loc. cit.*) that such solutions have a concentric configuration or form of motion. It is now shown that certain crystalloids can be made to separate in globular forms by careful over-cooling, and it is therefore assumed that these solutions also possess a concentric structure.

T. M. L.

**Colloidal Salts as Membrane-formers in Dyeing.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1608—1622).—"Dyeing in the great majority of cases consists in the separation of colloidal salts on or in the fibre." Colours of low molecular weight and small dyeing power are also devoid of colloidal properties, and are converted into true dyes by means of a colloidal mordant, tannin, or an insoluble soap for basic colours, and a metallic hydroxide for acid colours. On the other hand, the azo-dyes of high molecular weight, which dye cotton without a mordant, are sparingly soluble colloids which either separate directly on the fibre or are 'salted out' into it.

Rosaniline hydrochloride, methyl-violet, and methylene-blue have a normal molecular weight in dry alcohol according to the boiling point method, but give values about twice as great in aqueous solution, thus giving an indication of feeble colloidal properties. Thus, rosaniline hydrochloride ( $M=337$ ) gave 330.5, 325, and 343.6 in alcohol, but 520.6, 589.9, and 617.0 in water; methyl-violet (407.9) gave 403.5, 403.5, and 421.1 in alcohol, but 804.5, 838.7, and 870.4 in

water; methylene-blue (319·8) gave 321·4 and 342·7 in alcohol, but 442 in aqueous alcohol, and 321·2, 492·4, and 530·5 in water.

The colloidal nature of tannin is shown by the freezing point of its aqueous solution, which gave  $M=1587$  and 1626, calculated value = 322; a diffusion experiment showed a similar result. The metallic hydroxides used as mordants are true colloids, as was shown by Graham, (*Annalen*, 1862, 121, 1). A colloidal solution containing 3·38 per cent. of ferric hydroxide and 0·098 per cent. ferric chloride was found to freeze within  $0\cdot001^{\circ}$  per cent. of the freezing point of pure water; on cooling to  $-16^{\circ}$ , the hydroxide separated in thin, glistening, dark red-brown flakes. A colloidal solution containing 0·5 per cent. of aluminium hydroxide had exactly the freezing point of pure water; on cooling to  $-16^{\circ}$ , the hydroxide separated in very lustrous, transparent films. The insoluble soaps of iron, chromium, aluminium, tin, and antimony are also regarded as colloids, since they are precipitated in "globomorphous" form. It is shown that methylamine palmitate acts like the alkali soaps and gives colloidal solutions; the palmitates, &c., of basic dyes are therefore regarded as insoluble soaps, and colloidal in nature. In support of this, it is shown that rosaniline caproate at first lowers the boiling point of water to a small extent, owing to the volatility of the caproic acid, but on adding a further quantity, a very slight rise is observed, corresponding with a molecular weight of at least 600. The colloidal nature of the tannates of rosaniline, methylene-blue, chrysoidine, auramine, and a number of other mordanted dyes is assumed from the "globomorphous" form in which they are precipitated.

It is further shown that benzopurpurin which dyes cotton directly, gives a value  $M=3000$ , the calculated value being 724. On the other hand, "diamine pure blue" gives only  $M=343$ , instead of 993. The colloidal nature of these dyes is, however, shown by the fact that whilst rosaniline hydrochloride, methyl-violet, and methylene-blue diffuse through parchment, benzopurpurin, benzazurin, and azo-blue are retained.

T. M. L.

**Angles of Contact between the Crystal Faces of Alum and its Saturated Solutions.** By A. ROTA (*Real. Accad. dei Linc.*, 1898, 7, 125—129).—In order to find a connection between the physical properties of a salt solution and the habit of the crystals separating from that solution, the author has determined the angle of contact between octahedral and cubic alum crystals and their saturated solutions. On allowing the solvent to evaporate from a solution of pure alum in distilled water, octahedral crystals are deposited; and by heating powdered alunite at  $300-400^{\circ}$ , and extracting with water the reddish substance thus produced, a solution is obtained which on purification yields cubic alum crystals. When the small crystals obtained by the spontaneous evaporation of the solutions were suspended in their respective mother liquors and allowed to grow, uneven faces giving irregular reflections were the result; so that before using the crystals, the faces were carefully polished, care being taken to keep the polished faces parallel to the original face. The method of measurement employed was that devised by Quincke, in which a drop of the liquid is placed on a plane surface of the solid and the angle between the light-ray reflected from the last element of the

liquid and that from the surface of the solid is read off on a goniometer. The angles of contact between an octahedral face and the octahedral and cubic solutions respectively were found to have the mean values  $10^{\circ} 16'$  and  $15^{\circ} 13'$ , and the values for a cubic face and the cubic and octahedral solutions respectively,  $10^{\circ} 22'$  and  $15^{\circ} 36'$ . From this, it is concluded that from any solution that form crystallises whose faces present the least angle of contact with the solution. T. H. P.

**Vacuum Regulator for Distillations Under Reduced Pressure.** By VICTOR AUGER (*Bull. Soc. Chim.*, 1898, 19, [iii], 731—733).—This apparatus consists of a reservoir separated into two parts by a horizontal indiarubber membrane, each enclosure being separately connected with the vacuum pump. The lower enclosure is connected with the distillation apparatus and contains the manometer; it is also fitted with an automatic arrangement for introducing variable quantities of air into the apparatus. This consists of a hollow nickel tube open at both ends, which is inserted horizontally into the reservoir by means of a flexible rubber stopper. The end of the tube within the apparatus is flattened out into a disc which is placed immediately below the indiarubber membrane; the outer end is bent downwards at right angles, and is pressed against an indiarubber pad by means of a counterpoise. At the commencement of the operation, the pressure in both compartments of the reservoir is diminished to the required extent, and the upper enclosure is then cut off from the pump, and as the pressure in the lower compartment continues to fall the membrane becomes convex on its lower side and presses down the disc of the hollow nickel tube. The outer end of this tube is consequently lifted off its indiarubber pad, and a certain quantity of air rushes into the lower receptacle, the pressures on each side of the diaphragm are equalised, and the membrane and nickel lever resume their original positions. This automatic introduction of air is repeated whenever the pressure in the lower receptacle falls below that in the upper; the apparatus maintains a constant pressure as long as the volume of gas removed by the pump exceeds that generated in the distillation. G. T. M.

**Modifications of the Geissler Pump.** By GIOVANNI GUGLIELMO (*Real. Accad. dei Linc.*, 1898, 7, 240—249).—The author describes further improvements in the modified form of Geissler's pump already devised by him (*Abstr.*, 1891, 524). The long, straight tube of the Geissler pump is replaced by a flexible rubber tube, the height of the instrument thus being diminished. To economise mercury and facilitate the manufacture of the pump, the bulbs are made of small capacity. The pressure of the rarefied air is measured by determining the pressure necessary to compress all the air in the receiver into the small capillary boring of the stopcock, the relation between the two pressures being previously found. T. H. P.





is very susceptible to attack, and brass is quickly corroded, the zinc being dissolved out, but the copper left intact. T. H. P.

**Sodium Aluminate as a means for the Removal of Lime and Suspended Matters from Water for use in Boilers.** By CHARLES F. MABERY and EDWIN B. BALTZLEY (*J. Amer. Chem. Soc.*, 1899, 21, 23—27).—The use of sodium aluminate is recommended for softening and clarifying water for boilers. This compound may be prepared by adding the proper amount of sodium hydroxide to a solution of aluminium sulphate, or by fusing clay with soda-ash; a definite quantity of it is well mixed with the water, which is then allowed to settle for from 12 to 24 hours. The precipitation of the acid calcium carbonate takes place according to the equation  $\text{CaH}_2(\text{CO}_3)_2 + \text{Na}_2\text{Al}_2\text{O}_4 + 2\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{Al}(\text{OH})_3 + \text{Na}_2\text{CO}_3$ ; the sodium carbonate produced decomposes the calcium sulphate in the water. The reactions with magnesium carbonate and sulphate are similar. The precipitated alumina causes any turbidity to rapidly settle, and experiments show that very hard and muddy waters can be successfully treated by this method. Comparative tests with sodium aluminate and sodium hydroxide show that the latter does not precipitate any of the magnesia from water, and, further, only removes about one-half as much lime as the former reagent. T. H. P.

**Stability of Solutions of Hypochlorous Acid in Presence of Alkalis.** By JULIUS THOMSEN (*J. pr. Chem.*, 1899, [ii], 59, 244—246).—Solutions of hypochlorous acid containing 1 mol. of acid to 200 mols. of water, and more dilute solutions, remain unaltered for several days, and solutions of the acid in excess of sodium hydroxide are equally stable. If, on the other hand, the acid is present in excess, decomposition soon takes place. These results agree with those obtained by Förster and Jorre (this vol., ii, 278). F. H. N.

**Colour of Compounds of Bromine and Iodine.** By J. H. KASTLE (*Amer. Chem. J.*, 1899, 21, 398—413).—The relationship of the halogens in regard to their power of producing coloured compounds is discussed, and it is shown that, in this respect, they follow the usual order, beginning with fluorine and culminating in iodine. The colour of their compounds is intimately connected with their stability, those compounds which are most highly coloured being, as a rule, most prone to decomposition, and, as, for example, in the case of phosphorus pentabromide, the colour deepens as the temperature more nearly attains that of recognised dissociation; it is suggested that even in the solid state these coloured halogen compounds may be slightly dissociated, the colour being due to greater or smaller quantities of free halogen, and it is only necessary to assume that the amount of dissociation is excessively minute, 0.000066045 gram of iodine being sufficient to impart a distinct yellow colour to 20 c.c. of water. Examples are cited, both of organic and inorganic compounds, to show how this assumption serves to explain the gradation in properties, both of groups of halogen compounds and of the alterations in colour of the individuals with rise or fall in temperature, and also the relationship between colour and stability. Lead bromide, for instance, although white

at ordinary temperatures, becomes yellow when heated, and its colour approaches more closely to that of the iodide as the temperature rises.  
A. L.

**Iodine in Sea Water.** By ARMAND GAUTIER (*Compt. rend.*, 1899, 128, 1069—1075).—The following method permits of the detection and estimation of 0.2 milligram of iodine per litre. The solution is treated with potassium carbonate as long as a precipitate is produced, rendered alkaline with caustic potash, and evaporated to the crystallising point. The whole is thoroughly mixed with 83 per cent. alcohol, the magma produced is filtered, and the filtrate evaporated to dryness. The residue is acidified with dilute sulphuric acid, neutralised with caustic potash, treated with 90 per cent. alcohol, and filtered. The filtrate contains the whole of the bromine and iodine in the state of bromides and iodides respectively; it is distilled with a concentrated solution of potassium dichromate, the liberated iodine received in a solution of caustic potash, and estimated by the author's method (*Compt. rend.*, 1899, 128, 644). When this process was applied to 5 litres of water taken from the surface of the open sea, metallic iodides could not be detected, and if present, cannot exceed 0.02 milligram per litre in amount. The residue left on treating sea water with dilute alcohol is mixed with caustic potash and fused in a nickel crucible, in order to decompose organic substances; the residue, after cooling with ice, is acidified with cold dilute sulphuric acid, and rendered feebly alkaline with caustic potash; the quantity of iodine present, estimated by the above process, amounts to 2.4 milligrams per litre. On filtering 5 litres of sea water through a filter of porous earthenware, a slimy residue is obtained which contains, besides animal and vegetable refuse, many species of rotifers and diatoms; it amounts to 10 milligrams per litre, and when fused with caustic potash and treated in the manner described above yields 0.52 milligram of iodine. The residue obtained on evaporating the filtrate to dryness is also fused with potash; the iodine present amounts to 1.8 milligrams per litre. These results indicate that water taken from the surface of the sea contains no metallic iodides, and that the whole of the iodine exists in organic compounds, four-fifths being contained in soluble compounds and the remainder forming part of the substance of the infusoria inhabiting the superficial layers of the ocean.  
G. T. M.

**Oxidising Action of Alkali Periodates.** By E. PÉCHARD (*Compt. rend.*, 1899, 128, 1101—1104).—The sodium periodate,  $\text{NaIO}_4$ , is acid to litmus, but neutral to methyl-orange, so that the salt may be estimated by titration with sulphuric acid using the latter indicator. The iodates and periodates are generally supposed to have similar oxidising properties, but in some cases they exhibit very marked differences. Sodium periodate reacts like a compound of the iodate and active oxygen; it gives all the reactions produced by ozone, tarnishing silver, oxidising thallous oxide, and decolorising indigo.

Iodates may be estimated by their oxidising action on oxalic acid in presence of sulphuric acid; periodates oxidise this reagent with extreme slowness, the action being comparable with that of ozone on the same substance. On adding manganous sulphate to the solution,

the periodate, like ozone, oxidises the manganous salt to manganese dioxide, whereon this substance and the iodate which results from the action are simultaneously reduced by the oxalic acid. When a periodate is added to an acid solution of ferrous sulphate, one atom of oxygen from the molecule of periodate at once oxidises a portion of the iron salt; the iodate produced has an oxidising action on ferrous salts in acid solutions, but the reaction proceeds very slowly, so that it is possible by a rapid titration to determine the active oxygen derived from the periodate. In alkaline solutions of ferrous salts, the active oxygen of the periodates alone reacts; iodates have no oxidising effect under these conditions. Similar results are obtained with solutions of sodium arsenite, and all these reactions may be employed in estimating periodates. A solution of disodium periodate,  $\text{Na}_2\text{H}_3\text{IO}_6$ , slowly decomposes hydrogen peroxide, its action being similar to that of caustic soda. A neutral solution of the mono-sodium salt decomposes hydrogen peroxide; oxygen is evolved, one-half of which is derived from the periodate and the other half from the peroxide,  $\text{NaIO}_4 + \text{H}_2\text{O}_2 = \text{NaIO}_3 + \text{H}_2\text{O} + \text{O}_2$ ; when the solution is acidified with sulphuric acid both oxygen and iodine are liberated in accordance with the following equation:  $2\text{HIO}_4 + 7\text{H}_2\text{O}_2 = 8\text{H}_2\text{O} + \text{I}_2 + 7\text{O}_2$ .

These results indicate that in alkaline and neutral solutions (methyl-orange being employed as indicator) the periodates have an oxidising action which is not exhibited by the iodates and perchlorates, and it therefore appears probable that the periodates differ in constitution from the corresponding salts of these series. G. T. M.

**Properties of Liquid Sulphurous Anhydride.** By A. LANGE (*Zeit. angew. Chem.*, 1899, 275—277, 300—305).—The specific gravity and the coefficient of expansion of liquid sulphurous anhydride were determined at temperatures from  $13.3^\circ$  to  $92.3^\circ$  by heating a known weight of the liquid in an iron vessel of known volume and connected with a manometer until the liquid just filled the vessel, this point being accurately indicated by the sudden and very rapid rise of pressure. Tables showing the specific gravity and coefficient of expansion of the anhydride from  $-50^\circ$  to  $100^\circ$  are given. From determinations of the pressure produced by heating the vessel a few degrees beyond the temperature at which it becomes just filled with liquid, and the coefficient of expansion at this temperature, the coefficient of compressibility was calculated; it increases from 0.000132 at  $16.3^\circ$  to 0.000467 at  $92.1^\circ$ . A sample of ordinary commercial liquid sulphurous anhydride which contained 0.7 per cent. of water, attacked iron at temperatures above  $70^\circ$ , forming a solid crust of ferrous sulphite and thiosulphate, but the metal was not affected, or only very slightly, by the pure anhydrous substance. The importance of these observations in regard to the storing of the liquid in iron cylinders and its use in freezing machines is pointed out. E. W. W.

**Preparation of Tellurium.** By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1899, 21, 347—351).—On treating electrolytic slimes with concentrated hydrochloric acid, filtering through asbestos, and passing sulphurous anhydride into the clear filtrate, it is found that, contrary to

Keller's statement (Abstr., 1898, ii, 638), the tellurium is precipitated as well as the selenium.

When tellurium dioxide is heated with aluminium or magnesium, a violent reaction takes place; with aluminium, the telluride is formed, but with magnesium the action is so energetic as to prevent any of the products being collected. On heating the oxide with dry glucose or asphalte, a mass of coke is produced, from which it is difficult to obtain the tellurium; with oxalic acid, however, the metal readily fuses into a button.

Tellurium is precipitated when an aqueous solution of an alkali telluride is warmed with either grape sugar or cane sugar; in the latter case, an intermediate formation of purple alkali telluride takes place.

T. H. P.

**Formation of Azoimide.** By SIMEON TANATAR (*Ber.*, 1899, 32, 1399—1400).—A benzene solution of nitrogen chloride containing about 3·3 per cent. of the latter reacts with an aqueous solution of hydrazine sulphate to form azoimide, as much as 36 per cent. of the theoretical yield being obtained when the two solutions are shaken together and aqueous caustic soda added at intervals. With the exception of the method proposed by Wislicenus, this is the best process for the preparation of the acid.

A. H.

**Preparation of Fuming Nitric Acid.** By LUDWIG VANINO (*Ber.*, 1899, 32, 1392—1393).—When formaldehyde is added to concentrated nitric acid, a rapid evolution of nitric peroxide occurs, but the exact quantitative relations have not yet been determined. Fuming nitric acid may be prepared by passing the gases thus evolved into nitric acid, or more directly by adding the solid form of paraformaldehyde to nitric acid, no organic products remaining in the acid. The presence of hydrochloric acid or of chlorine greatly hinders the reaction, whilst hydrogen peroxide appears to prevent it completely.

A. H.

**Behaviour of Nitric Peroxide with Sulphuric Acid and Nitric Acid.** By GEORG LUNGE and E. WEINTRAUB (*Zeit. angew. Chem.*, 1899, 393—402, 417—424).—From three series of experiments in which sulphuric acid of various strengths was treated with (a) nitrosylsulphuric acid, (b) nitric peroxide, and (c) nitric acid and nitric peroxide, and a fourth in which nitric acid was mixed with nitrosylsulphuric acid, the following conclusions were reached. (1) When nitric peroxide is mixed with sulphuric acid, nitrosylsulphuric acid and nitric acid are formed, but since the reverse change may also occur, the mixture contains all four compounds, and a state of equilibrium is attained. (2) When sulphuric acid of sp. gr. 1·84 is employed, the conversion of nitric peroxide into nitrosylsulphuric and nitric acids is the main reaction, the reverse reaction only coming into prominence when the quantity of sulphuric acid is small. (3) The affinity of sulphuric acid for nitric peroxide decreases rapidly as the amount of water is increased, hence with sulphuric acid of sp. gr. 1·65 a large proportion of the peroxide remains uncombined, although the quantity of nitric acid present is small. (4) In the manufacture of sulphuric acid, the nitric peroxide is almost completely converted into nitrosylsulphuric acid and

nitric acid, owing to the presence of a large excess of sulphuric acid, and similarly, nitrous fumes are completely absorbed by a large excess of sulphuric acid.

E. W. W.

**Action of Metals on Nitric Acid.** By PAUL C. FREER and GEORGE O. HIGLEY (*Amer. Chem. J.*, 1899, 21, 377—392. Compare Abstr., 1893, ii, 272, &c.).—The action of pure iron wire on nitric acid of various strengths was examined. With dilute acid, the products were nitric peroxide, nitric oxide, nitrous oxide, nitrogen, and ammonia, in proportions which varied both with the concentration and the amount of acid used. The results obtained with dilute acid (sp. gr. 1.20—1.03) were not in harmony with those of Acworth and Armstrong (*Trans.*, 1877, 32, 79), owing to the fact that these workers made no determinations of the nitric peroxide and ammonia which were formed.

Silver, copper, and iron have a similar action on strong nitric acid (sp. gr. 1.40—1.35), the products being nitric peroxide and nitric oxide, and the curves obtained for silver and copper were practically identical. The specific action of these three metals is only observed when the dilution is considerable, hence the non-ionised acid acts merely as an oxidising agent; in this case, nitric peroxide is probably the first product, and nitric oxide is obtained only as the result of a secondary change due to the action of water on the peroxide, this view being confirmed by the observation that the relative proportions of these two gases vary with the mass of the acid present.

Silver and copper have substantially the same action on nitric acid of medium strength (sp. gr. 1.2), giving 10 per cent. of nitric peroxide and 90 per cent. of nitric oxide; with lead, however, the products are nitrous oxide (40 per cent.), nitric oxide (50 per cent.), and nitric peroxide (only 2.5 per cent.). The metals examined may therefore be ranged in the following order in regard to their action on dilute nitric acid, beginning with the weakest: silver, copper, lead, and iron, but in stronger acid, lead acts more energetically than iron.

In order to throw light on the mode of action of metals on nitric acid, the liquid was submitted to electrolysis, cathodes of platinum, silver, lead, and copper of equal area being employed. It is concluded that the activity of electrolytic hydrogen depends on the electrode on the surface of which it is liberated; that electrolytic hydrogen with cathodes of copper or silver effects the reduction of the acid in proportion to the current density; that nitric acid of sp. gr. 1.05, when electrolysed with cathodes of silver or lead with equal current densities yields the same products, namely, nitrogen and ammonia in about the same proportions, but when these metals dissolve in acid of this strength, the products are widely different, both qualitatively and quantitatively.

Lead, which reduced nitric acid of sp. gr. 1.05 much more completely than does copper yielding about five times as much nitric oxide when made the cathode of an electrolytic cell, has a far feeblere action, and yields only about one-third of the amount of ammonia given by the latter.

Since, in the electrolysis of nitric acid with a constant current the action of metal ions is excluded, and the reduction must be effected by

hydrogen ions in contact with the metal, it follows that the widely different effects observed on dissolving metals in nitric acid must be attributed to the different deoxidising properties of the metals themselves, and not to the effect of nascent hydrogen. A. L.

**Dissociation of Phosphorus Pentabromide in Solution in Organic Solvents.** By J. H. KASTLE and W. A. BEATTY (*Amer. Chem. J.*, 1899, 21, 392—398).—Many bromine compounds of the most diverse types are yellow in the solid state, and dissolve in inert media to form solutions which have colours closely resembling those of bromine solutions. The idea suggested itself that in such solutions the compounds were either wholly or partly dissociated or decomposed. Such a compound is found in phosphorus pentabromide, which is readily obtained in a pure state as yellow, rhombic prisms, which, when heated in a sealed tube, melt, forming a dark red liquid; this, when further heated, is dissociated, giving dark red vapours of bromine; it forms dark red solutions in carbon bisulphide, chloroform, or carbon tetrachloride, and these have been subjected to colorimetric comparisons with solutions of bromine in the same liquids.

The results appear to show that in carbon bisulphide the compound is completely dissociated into phosphorus tribromide and free bromine at dilutions varying between  $N/100$  and  $N/1000$ , and that it is not a non-reversible decomposition is indicated by the fact that the red and yellow modifications of the pentabromide may be obtained on evaporation. Further support is obtained for this view from the fact that the addition of tribromide to the solutions causes them to become lighter in colour, and that addition of carbon bisulphide to the solution of the pentabromide in tribromide causes a deepening of the colour.

In carbon tetrachloride, the pentabromide appears to be dissociated to the extent of 90 per cent. at dilutions between  $N/40$  and  $N/400$ ; no sufficient reason for the difference in behaviour of carbon bisulphide and carbon tetrachloride has as yet been found, but it is thought that it may be connected with the greater solubility of the substance in the former liquid. A. L.

**Preparation of Graphitic Acid. II.** By LUDWIG STAUDENMAIER (*Ber.*, 1899, 32, 1394—1399. Compare Abstr., 1898, ii, 472).—A small amount of graphitic acid can be rapidly prepared to illustrate a lecture by bringing a mixture of carefully prepared graphite with 50—60 times its weight of potassium chlorate into a mixture of pure sulphuric acid with half its volume of nitric acid, the whole being gradually heated up to  $80^{\circ}$ . The green intermediate product is thus formed, and the mass is then poured into a concentrated solution of potassium permanganate and heated until the whole of the latter is decomposed. The graphitic acid is then left as an insoluble, yellow mass. Intumescent graphite (Ceylon graphite) must be previously brought along with an equal weight of potassium chlorate, into a mixture of nitric and sulphuric acids, gradually heated to  $100^{\circ}$ , and then washed and strongly heated; the resulting voluminous mass is then washed and all the lighter portions again heated strongly, after which it is submitted to the final oxidation. Non-intumescent

varieties of graphite, such as that from Bohemia, are simply fused with caustic potash, washed, and finely ground.

Large amounts of graphitic acid may be prepared in a very similar manner by simply allowing the graphite to remain for some days at atmospheric temperature in the mixture of acids, potassium chlorate being added at intervals until the green compound is formed. As much as 250 grams of graphite have been oxidised in one operation by this method, which is quite free from danger, provided that the mass is occasionally stirred, in order to prevent any great rise of temperature or any accumulation of chlorine peroxide. A. H.

**Percarbonates.** By SIMEON M. TANATAR (*Ber.*, 1899, 32, 1544—1546).—Sodium percarbonate,  $\text{Na}_2\text{CO}_3 + 1\frac{1}{2}\text{H}_2\text{O}_2$ , is precipitated as a fine, crystalline powder on adding alcohol (3 vols.) to a mixture of sodium carbonate (7.5 grams) and hydrogen peroxide (100 grams) which has stood for from 5 to 10 minutes. Like all similarly constituted compounds, it gradually decomposes in aqueous solution, forming hydrogen peroxide and sodium carbonate; with acids, carbonic anhydride is evolved, and the solution contains hydrogen peroxide which can be extracted with ether; halogen acids are oxidised with separation of the halogen; when heated at  $100^\circ$ , oxygen is evolved, unaccompanied by carbonic anhydride. The heat of decomposition of the salt, determined by adding to its *N*/10 solution a *N*/10 solution of nitric acid, gave 7.210—7.260 Cal., the heat of decomposition of sodium carbonate being 5.33 Cal. The salt dissolves in water with a heat absorption of about 3.9 Cal.

By employing twice as much hydrogen peroxide in the above reaction, the salt  $\text{Na}_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}_2 + \text{H}_2\text{O}$  is obtained.

Potassium percarbonate has not as yet been obtained in a pure condition.

Whether these compounds are in reality salts of percarbonic acid, or whether they are merely double compounds of the carbonate and hydrogen peroxide in which the latter plays the part of water of crystallisation is, in the author's opinion, still open to question, although their thermochemical behaviour and the non-formation of similar compounds from other salts containing water of crystallisation seems to favour the former view. J. F. T.

**Probable Presence of Coronium and New Elements in the Solfatara of Pozzuoli and Vesuvius.** By RAFFAELE NASINI, FRANCESCO ANDERLINI, and ROBERTO SALVADORI (*Real. Accad. dei Linc.*, 1898, 7, 73—74).—The gas emitted from the solfatara of Pozzuoli, besides containing argon, shows in its spectrum a brilliant line having the wave-length 531.5—531.6; this corresponds exactly with the coronal line 1474 *K* belonging to an undiscovered element, coronium, which is lighter than hydrogen, and has never before been detected in any terrestrial body. Also lines with the following wave-lengths are present: 653.5, 595.5, and 536.2; the line 595.5 is found in the spectra of gases from some of the Vesuvius fumaroles, and, in addition, the lines 769.5, 631.8, 572.5, 536.5, and 441.5. None of these belong either to the spectrum of argon or that of helium; some of them coincide with or approximate to unimportant lines of the



spectra of iron, potassium, titanium, and mercury, but the presence in the gas of these elements is very improbable under the experimental conditions employed. The line of 572.5 wave-length, which is almost coincident with a line of the nitrogen spectrum, cannot be attributed to that element, since of all the nitrogen lines it is the only one visible. The authors are of opinion that besides coronium, other new gaseous elements are present. T. H. P.

**New Method of Preparing Cæsium.** By HUGO ERDMANN and ALBERT E. MENKE (*J. Amer. Chem. Soc.*, 1899, 21, 259—262).—Cæsium alum is converted by means of baryta into the sulphate and thence into the hydroxide. The hydroxide is heated with magnesium in an iron tube in a current of hydrogen gas, and the cæsium is collected under paraffin in almost a theoretical yield. T. M. L.

**Specific Gravity of Cæsium.** By ALBERT E. MENKE (*J. Amer. Chem. Soc.*, 1899, 21, 420—421).—By weighing highly purified cæsium in hydrogen and then under paraffin, a mean value of 2.40003 is found for its specific gravity. This number changes the atomic volume from 70.6, the usually accepted value, to 55.3, which is less than that of rubidium. The accuracy of the value adopted for the specific gravity of the latter metal is questioned. The results obtained confirm Beketoff's numbers. T. H. P.

**Luminous Phenomena Produced by Ammonium Salt and Fused Potassium Nitrite.** By DONATO TOMMASI (*Compt. rend.*, 1899, 128, 1107).—When powdered ammonium nitrate is scattered over fused potassium nitrate, the whole surface of the molten salt becomes studded with phosphorescent particles; if a single crystal of the ammonium salt be added, it takes the form of an incandescent globule surrounded by a rotating phosphorescent ring; after a few seconds the globule bursts, giving rise to a violet flame. Ammonium chloride and sulphate behave similarly, but the luminous effect is less pronounced. G. T. M.

**Silver Peroxysulphate.** By EDUARD MULDER (*Chem. Centr.*, 1899, i, 16; from *Verh. Kon. Akad. Wetensch. Amsterdam*, 1898).—Silver peroxysulphate,  $5\text{Ag}_2\text{O}_2 \cdot 2\text{Ag}_2\text{SO}_7$ , is obtained as a black, crystalline precipitate by electrolysing a half-saturated solution of silver sulphate, the formation of free sulphuric acid which decomposes this compound being avoided by continually neutralising the liquid with silver carbonate. The composition of the compound was ascertained by boiling it with water, estimating the quantity of oxygen liberated by the decomposition of the sulphate  $\text{Ag}_2\text{SO}_7$ , and determining the residual peroxide by dissolving in nitric acid. E. W. W.

**Caustic Lime in Ancient Masonry.** By GEORGES ARTH (*Bull. Soc. Chim.*, 1898, 19, [iii], 717—718).—A portion of the old walls of Nancy built in the 17th century was found to contain in its interior several small cavities filled with hydrated lime. One fragment weighing 40 grams contained 57.5 per cent. of calcium hydroxide and only a trace of calcium carbonate. G. T. M.

**Action of Manganese in Producing Phosphorescence of Strontium Sulphide.** By JOSÉ R. MOURELO (*Compt. rend.*, 1899, 128, 1239—1241).—Strontium sulphide, produced by igniting a mixture of pure strontium carbonate with flowers of sulphur and oxide of manganese, prepared by heating the carbonate, are not phosphorescent separately, but when a mixture of strontium carbonate (100 pts.), flowers of sulphur (33 pts.), and manganese carbonate (0.15 pt.) is heated to redness, a greyish-white mass is obtained, which, after a short exposure to diffused daylight, exhibits a persistent green phosphorescence, the colour of which differs markedly from the yellowish-green tint obtained with phosphorescent strontium sulphide. The most intense effect is obtained by adding sodium carbonate (1.4 pts.) and fused sodium chloride (0.85 pt.) to the above ingredients and igniting the mixture at bright red heat for 3 hours; the cooled product, after exposure to light, phosphoresces strongly, the shade of green exhibited being quite different from that developed when basic bismuth nitrate is the active agent. G. T. M.

**Magnesium Phosphide.** By HENRI GAUTIER (*Compt. rend.*, 1899, 128, 1167—1169).—Magnesium phosphide,  $Mg_3P_2$ , can be obtained by the direct combination of phosphorus vapour and magnesium in an atmosphere of hydrogen, and forms small, brilliant, dark greenish-grey crystals, which alter rapidly in moist air, and can only be kept in sealed tubes. Dry air and oxygen are without action at the ordinary temperature, but the phosphide burns in oxygen at a dull red heat, and is converted into magnesium phosphate. The phosphide burns brilliantly when heated in chlorine, and also in bromine and iodine vapours at somewhat higher temperatures. Hydrochloric acid decomposes it with liberation of hydrogen phosphide; concentrated sulphuric acid slowly converts it into magnesium sulphate and phosphoric acid; nitric acid oxidises it with incandescence, forming magnesium nitrate and phosphoric acid. Water very readily decomposes the phosphide, with production of magnesium hydroxide and pure hydrogen phosphide. C. H. B.

**Halogen Lead Salts.** By VICTOR THOMAS (*Compt. rend.*, 1899, 128, 1234—1236. Compare *Abstr.*, 1898, ii, 585, and this vol., ii, 278).—A *lead chlorobromide* having the composition  $3PbCl_2, PbBr_2$  is produced by dissolving lead chloride and potassium bromide in water. The double salt is decomposed by water into its components; hydrochloric acid converts it into lead chloride, and hydrobromic acid into the bromide. When the chloriodide,  $PbICl$ , is treated with bromine, it gives rise to a *chlorobromide*,  $PbBrCl$ , which is obtained in colourless needles; its properties resemble those of the preceding double salt, and it is converted into lead iodide by boiling with hydriodic acid. Definite chlorobromides could not be isolated from mixtures of hydrobromic acid and lead chloride, hydrochloric acid and lead bromide, and lead bromide and chloride. A *lead bromiodide* having the composition  $3PbBr_2, PbI_2$  is obtained by saturating a solution of lead bromide with lead iodide and subsequently cooling; the same compound is produced when lead bromide and potassium iodide are dissolved in water and the solution kept at 50—65°; as the temperature falls below 50°, the

amount of admixed lead bromide increases, whilst above  $65^{\circ}$  the double salt is contaminated with lead iodide. G. T. M.

**Apparatus for the Purification of Mercury.** By WILHELM PALMAER (*Ber.*, 1899, 32, 1391—1392).—Mercury is allowed to fall through dilute nitric acid in very fine streams, which are obtained by causing the metal to leave the vessel containing it by way of a number of long, narrow depressions, about 0.25 mm. in breadth, cut into the surface of a glass rod which is ground into the narrow lower extremity of the mercury reservoir. A. H.

**Displacement of Mercury by Hydrogen.** By ALBERT COLSON (*Compt. rend.*, 1899, 128, 1104—1106).—When dried, powdered, yellow mercuric oxide is heated at  $100^{\circ}$  in tubes filled with hydrogen, it is reduced to the metal, the amount of hydrogen absorbed being directly proportional to the quantity of oxide, and to the time of the experiment. The rate of absorption is proportional to the cube root of the pressure, and is five times greater for the yellow oxide than for the red modification; in other respects, the results obtained with the two varieties of mercuric oxide are quite comparable. Hydrogen has no reducing action on mercurous oxide at  $100^{\circ}$ ; on the other hand, this substance at the same temperature rapidly absorbs oxygen.

Mercuric chloride is not acted on by hydrogen at  $100^{\circ}$ , but the corresponding nitrate and sulphate are readily reduced, the latter oxy-salt being converted into mercurous sulphate and sulphuric acid. This reaction is slow at first, but afterwards proceeds more rapidly, the presence of free sulphuric acid facilitating the reduction. Sulphurous anhydride is simultaneously produced, and is probably derived from the mercurous sulphate,  $\text{Hg}_2\text{SO}_4 + \text{H}_2 = \text{Hg}_2\text{O} + \text{SO}_2 + \text{H}_2\text{O}$ ; the oxide produced combines with some of the free sulphuric acid and regenerates mercurous sulphate.

Mercurous nitrate, when heated at  $100^{\circ}$  with hydrogen, decomposes in the following manner:  $\text{Hg}_2(\text{NO}_3)_2 + 2\text{H}_2 = 2\text{NO} + 2\text{HgO} + 2\text{H}_2\text{O}$ ; the hydrogen reduces the acid radicle, and at the same time brings about an oxidation of the mercury radicle from the *ous* to the *ic* condition. At  $100^{\circ}$ , mercurous nitrate absorbs oxygen, giving rise to mercuric compounds; on the other hand, mercuric salts at the same temperature are easily reduced by hydrogen, and water is produced; it may therefore be inferred that the presence of mercuric salts lowers considerably the temperature of combination of hydrogen and oxygen.

G. T. M.

**Chemistry of Mercury.** By HEINRICH LEY and H. KISSEL (*Ber.*, 1899, 32, 1357—1368).—The only compounds of bivalent mercury which show a tendency to electrolytic dissociation are those in which the metal is directly united with oxygen. Thus the chloride and bromide possess a very low molecular conductivity, and that of the cyanide is even lower. In the same way, mercury acetamide and mercury succinimide also have a very low conductivity, and in aqueous solution act as weak bases which are decomposed by hydrochloric acid. The acetamide compound can, in fact, be titrated with hydrochloric acid in presence of methyl-orange. Mercury glycocine closely resembles

the acetamide compound in its behaviour, and has therefore probably the constitution  $\text{Hg}(\text{NH}_2\text{C}(\text{O})\text{CH}_3)_2$ .

The salts of mercury with acetic, propionic, glycollic, and monochloroacetic acids undergo a considerable hydrolytic decomposition in aqueous solution, which is rendered evident by the agreement of their conductivities with those of the corresponding acids, and by the fact that the hydrogen ions present are capable of bringing about the inversion of sugar, &c. Mercury perchlorate also undergoes hydrolytic decomposition in solution. This behaviour of the mercury compounds may be utilised for ascertaining the constitution of various derivatives of the metal. Mercuric nitrite has the conductivity of an oxygen compound of mercury, the value for the conductivity showing that nitrous acid must be of about the same strength as acetic acid. The mercury derivative of methylnitramine crystallises in hard, colourless needles, and in solution has the properties of an oxygen compound of mercury, so that its constitution is most probably  $\text{Hg}(\text{O}\cdot\text{NMe}\cdot\text{ON})_2$ .

Mercuric fulminate behaves electrolytically in an analogous manner to the cyanide, and it is, therefore, probably not an oxygen derivative as supposed by Nef. The cyanide also resembles the fulminate in the fact that it is readily converted by sodium amalgam into the sodium salt, which is strongly dissociated.

Mercury nitroform is colourless in the solid form and yields colourless solutions in ether, benzene, &c., whilst its solution in water is yellow and has a fairly high conductivity, which indicates that both electrolytic dissociation and hydrolytic decomposition have occurred. It therefore appears that both nitroform itself and its mercury derivative in the solid form are true nitro-compounds, whereas in solution they both have the isomeric structure.

A. H.

**Formation of Red Mercuric Sulphide in the Wet Way.** By UGO ALVISI (*Real. Accad. dei Linc.*, 1898, 7, 97—98).—When the following substances are suspended in solutions of yellow ammonium sulphide, they are converted into red mercuric sulphide: (1)  $\text{Hg}(\text{EtS})_2$ , on shaking with the ammonium sulphide solution, this compound is immediately changed into the sulphide; (2)  $\text{HgCl}\cdot\text{EtS}$ , this requires a longer time, becoming first black and then red; (3)  $\text{HgCl}_2\cdot\text{Et}_2\text{S}$  and (4)  $\text{Hg}_2\text{Cl}_2$  are converted very slowly into the sulphide, passing first into an intermediate, black, crystalline compound; the reaction, which takes place in the cold, is accompanied by the separation of ethylic sulphide.

On passing hydrogen sulphide through boiling water in which mercury mercaptide is suspended, the mercaptide assumes first a reddish colour, then becomes black, and finally reddish again, large quantities of mercaptan being meanwhile evolved. Analysis of the red compound shows it to be mercuric sulphide, which is also obtained by passing hydrogen sulphide into a hot acidified solution of mercury mercaptide in alcohol.

T. H. P.

**A Crystallised Double Perceric Carbonate.** By ANDRÉ JOB (*Compt. rend.*, 1899, 128, 1098—1099. Compare this vol., ii, 291 and 334).—A solution of ceric peroxide in potassium carbonate containing

carbonic acid may be kept for several months without undergoing alteration ; by spontaneous evaporation at ordinary temperature, it deposits the double carbonate,  $\text{Ce}_2\text{O}_3(\text{CO}_3)_3, 4\text{K}_2\text{CO}_3 + 12\text{H}_2\text{O}$ , which separates in blood-red crystals. This substance, when dissolved in dilute sulphuric acid, yields carbonic anhydride, oxygen, hydrogen peroxide, and potassium cerous sulphate. A brown liquid having all the characters of a solution of a perceric salt is obtained on dissolving the double carbonate in a dilute solution of potassium carbonate. The crystals of the double carbonate become anhydrous when heated to  $110^\circ$ , but undergo no further decomposition when the temperature is raised to  $200^\circ$ ; at  $210^\circ$ , evolution of oxygen commences, and as the temperature rises, the rate of evolution increases; at  $300^\circ$ , carbonic anhydride is liberated, and the decomposition is complete in 1 hour at  $360^\circ$ ; the residue then consists of a yellow ceric potassium carbonate having the composition  $\text{Ce}_2\text{O}_3, \text{CO}_3, 4\text{K}_2\text{CO}_3$ . The double perceric carbonate is also produced, together with the yellow ceric salt by agitating a solution of cerous nitrate and potassium carbonate in the presence of atmospheric oxygen.

G. T. M.

**Impurities in Aluminium.** By ADOLPHE MINET (*Compt. rend.*, 1899, 128, 1163—1167).—The aluminium now made is of a relatively high degree of purity, the iron and silicon, which together amount to considerably less than 1 per cent., being mainly derived from the electrodes or from the walls of the furnace. One of the best forms of furnace is a parallelepiped of iron lined with carbon, and provided with an outlet below the cathode for the continuous removal of the aluminium. The anode and cathode are quite independent of the furnace; if the latter is made to play the part of the cathode, it is liable to be rapidly attacked and the aluminium produced becomes comparatively impure.

C. H. B.

**Absorption. IV. Colloidal Ferric Oxide.** By JACOBUS M. VAN BEMMELEN (*Zeit. anorg. Chem.*, 1899, 20, 185—211; see also *Abstr.*, 1897, ii, 137; 1898, ii, 220; this vol., ii, 12 and 84).—The elimination, reabsorption, and the repeated elimination of the water of the hydrogel of ferric oxide, prepared from a dilute ferric solution and ammonia, has been examined in the case of samples; (i) freshly prepared; (ii) air-dried and many years old; (iii) kept under water for a considerable time. The results agree with those obtained for the hydrogels of silicic acid and copper oxide. The hydrogel has the properties of an amorphous, colloidal substance, it forms no definite hydrate, and the percentage of water depends on the molecular state due to the conditions under which it is formed, and the modifications due to drying, time, the action of water, temperature, &c. When products are obtained containing  $4\text{H}_2\text{O}$ , or a less number of water molecules corresponding with a chemical hydrate, this is due to chance. The experiments again prove that in an amorphous substance the physical molecular condition, and consequently the composition, alters in a perfectly continuous manner. This alteration is very slow at ordinary temperatures, and is accelerated at higher temperatures.

E. C. R.

**Iron Silicides with a High Percentage of Silicon.** By GUILLAME J. L. DE CHALMOT (*J. Amer. Chem. Soc.*, 1899, 21, 59—66).—By heating a mixture of river sand with finely ground iron ore and coke in the electric furnace, the author has obtained iron silicides containing from 12 to 46 per cent. of silicon. No flux is required, but an excess of silica must be employed, as it readily volatilises and is carried away by the furnace draught; very little slag is formed, and the silicide is run out in a molten state. Iron silicides containing from 25 to 50 per cent. of silicon consist of a mixture of two definite compounds. The first of these,  $\text{Fe}_3\text{Si}_2$ , with 25 per cent. of silicon, separates in large, well-developed crystals on allowing molten silicides containing from 25 to 28 per cent. of silicon to slowly solidify. The second compound,  $\text{FeSi}_2$ , containing 50 per cent. of silicon, the author obtains as a residue on partially dissolving a silicide with 39 per cent. of silicon in dilute hydrofluoric acid; it forms a grey, crystalline, non-magnetic powder. A compound with more than 50 per cent. of silicon could not be obtained, any excess over this proportion separating in small, black crystals. The silicide,  $\text{FeSi}$ , previously described, is probably not present in the silicides obtained by the author. Iron silicides are always crystalline and of a white or grey colour, some of them being capable of taking a very high polish. They are very hard and brittle, thus forming valuable abrasives, and are good conductors of electricity. Air and water are without action on them, and they are only slowly attacked by all acids with the exception of hydrofluoric acid. The melting point rises and the specific gravity falls with an increase in the amount of silicon. Compounds with little silicon cast well, but with larger proportions, the castings tend to crack on cooling. T. H. P.

**Atomic Weight of Nickel.** By THEODORE W. RICHARDS and ALLERTON S. CUSHMAN (*Zeit. anorg. Chem.*, 1899, 20, 352—376. See also Abstr., 1898, ii, 228).—In continuation of their work on the atomic weight of nickel, the authors have determined the weight of nickel obtained from a weighed quantity of nickel bromide by reducing it in a current of hydrogen. The apparatus employed and the method of conducting the analysis are the same as previously described. A careful examination of the nickel bromide shows that it contains 1/10 per cent. of sodium bromide, which is derived from the porcelain tube employed in its preparation, and the authors have been unable to eliminate this impurity. The sodium bromide was therefore determined in each sample of the reduced nickel by extraction with water and precipitating with silver. Weighing the sodium bromide left by evaporation of the extract to dryness gives inaccurate results, since the authors find that, by the action of water on the reduced nickel, a small quantity of nickel is dissolved as colloidal hydroxide. The complete analysis of nickel bromide gave 26.824 per cent. Ni, 73.062 per cent. Br combined with the nickel, 0.089 per cent. Br in the impurities, and 0.025 per cent. Na = 100.000. The mean of eight experiments gave as the atomic weight  $\text{Ni} = 58.709$  [ $\text{O} = 16$ ], the extreme values being 58.696 and 58.719. The mean of these and the authors' previous determinations gave as the atomic weight  $\text{Ni} = 58.706$ . E. C. R.

**Action of Hypophosphorous Acid on Molybdic Acid.** By CLARENCE EBAUGH and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 384—386).—In studying the reduction of molybdic acid by means of hypophosphorous acid, definite volumes of solutions of ammonium molybdate and of hypophosphorous acid of known strength were mixed, water added to the extent of three times the volume of the mixture, and the liquid boiled for a fixed time. After cooling, the solution was re-oxidised by titration with standard permanganate, the volume required indicating the amount of reduction effected by the hypophosphorous acid. The results show that the molybdic acid suffers reduction to the pentoxide ( $\text{Mo}_2\text{O}_5$ ), but that the method cannot be used for the accurate estimation of molybdenum. T. H. P.

**Tungsten.** By ALFRED STAVENHAGEN (*Ber.*, 1899, 32, 1513—1516).—The author gives details of the method by which he has prepared elementary tungsten with the object of studying its physical properties; the source of the metal was tungstic acid, aluminium borings being employed as the reducing agent. Fused tungsten which has been allowed to solidify has a sp. gr. 16.6; it is sufficiently hard to cut glass, and remains solid in the oxyhydrogen flame. The metal is indifferent towards acids and aqua regia, but dissolves slowly in fused potassium hydroxide, liberating hydrogen. M. O. F.

**Atomic Weight of Tungsten and Preparation of Sodium Pertungstate by means of the Electric Current.** By GEORGE EDWARD THOMAS (*J. Amer. Chem. Soc.*, 1899, 21, 373—381).—An attempt was made to determine the atomic weight of tungsten by measuring the loss of water of crystallisation (2 mols.) on heating at 268—295° crystals of sodium tungstate obtained both from scheelite and from wolframite. Owing, however, to the great difference between the molecular weight of water and the atomic weight of tungsten, and also to slight losses due to volatilisation of the material, the method does not give good results.

By electrolysing a 30 per cent. sodium tungstate solution slightly acidified with acetic acid, sodium pertungstate is formed, but the author was unable to isolate it in a pure condition. T. H. P.

**Tungsten Pentabromide.** By ED. DEFACQZ (*Compt. rend.*, 1899, 128, 1232—1234).—Tungsten pentabromide is obtained in well-defined, fern-like aggregates of dark needles with a green reflex, by passing dry hydrogen bromide over tungsten hexachloride heated at 300°; it is very hygroscopic, yielding the blue oxide on treatment with water and dilute acids; it is soluble in the following organic solvents: carbon tetrachloride, chloroform, bromoform, ether, alcohol, turpentine, and benzene. It is decomposed by oxygen into a mixture of oxybromides and tungstic acid, and when heated with chlorine, sulphur, or phosphorus, yields the chloride, sulphide, or phosphide respectively; the latter compounds are also produced by the action of hydrogen sulphide and hydrogen phosphide; it may be volatilised without decomposition in an atmosphere of carbonic anhydride. Concentrated solutions of hydrofluoric and hydrochloric acids dissolve the pentabromide, the latter reagent giving an indigo blue solution;

fuming hydrobromic acid partly dissolves the substance, concentrated sulphuric acid has no action in the cold. Nitric acid oxidises the bromide to tungstic acid, and the reaction is utilised in analysing the substance. Hydrogen iodide at  $400^{\circ}$  decomposes the bromide, giving rise to an iodide. The pentabromide is readily attacked by alkalis, whether molten or in solution, and by fused alkali nitrates, carbonates, and bisulphates.

G. T. M.

**Reaction between Some Salt Solutions and an Alkaline Solution of Antimony Trioxide.** By M. C. HARDING (*Zeit. anorg. Chem.*, 1899, 20, 235—239).—A black precipitate, containing platinum and antimony approximately in the ratio 1Pt:2Sb, is obtained by adding a dilute solution of hydrogen platinumchloride to excess of an alkaline solution of antimony trioxide. When treated with dilute hydrochloric acid, it yields a residue of metallic platinum, and an equal quantity of platinum is dissolved.

An acid or alkaline solution of gold, when added to excess of an alkaline solution of antimony trioxide, gives a precipitate of aurous oxide containing from 6.5—26.0 per cent. of antimony. When a neutral solution of gold is employed, the precipitate contains gold and antimony, approximately in atomic proportion. When excess of gold solution is employed, the precipitate consists almost entirely of aurous oxide.

Mercuric and mercurous salts are converted into metallic mercury and mercurous oxide by excess of the antimony solution. If the mercury salt is in excess, then mercurous oxide is formed.

*Cupric antimonite*,  $\text{CuSb}_2\text{O}_4$ , is obtained by adding a dilute solution of copper sulphate to an excess of the alkaline antimony solution, or by adding copper sulphate to a solution of potassium antimonyltartrate in 8 per cent. aqueous potassium hydroxide; it is a green, crystalline powder, is soluble in hydrochloric, tartaric, or citric acids, and when heated in an open crucible at first evolves antimony oxide and then explodes, leaving a residue of antimony trioxide and copper oxide; when heated in a closed vessel, the residue contains metallic copper.

When treated with excess of the antimony solution, ferric chloride yields a red solution, which, on warming, deposits a brown precipitate containing varying proportions of ferric oxide and antimony trioxide. The red solution is very unstable, and is immediately decolorised when shaken with the carbonates of calcium, barium, strontium, magnesium, or lead.

An alkaline solution of antimony trioxide yields, with potassium permanganate, a precipitate containing manganese peroxide and antimony trioxide, reduces chromates with the formation of chromoxy-compounds, and with stannous chloride yields metallic antimony mixed with a small quantity of tin.

E. C. R.

**Antimony Pentasulphide.** By OTTO KLENKER (*J. pr. Chem.*, 1899, ii, 59, 150—194. Compare Bosek, *Trans.*, 1895, 67, 515; and Brauner, *ibid.*, 527).—The action of heat, of water, of tartaric acid, and of hydrochloric acid on antimony pentasulphide was investigated; the experiments showed the ease with which the



quinguevalent compound is converted into the black, crystalline trisulphide and then into antimonious oxide, the latter change occurring at a temperature of  $230^{\circ}$ , whilst the former is brought about by heating in an air-bath to  $150^{\circ}$ . Alcohol, benzene, and chloroform at the boiling temperatures extract as much sulphur from the pentasulphide as carbon bisulphide does, but in the latter case less time is required for the extraction. Boiling oil of turpentine also causes partial decomposition of the pentasulphide. F. H. N.

**Perniobic and Pertantallic Acids and their Salts.** By PETR G. MELIKOFF and L. PISSARJEWSKY (*Zeit. anorg. Chem.*, 1899, **20**, 340—351).—*Perniobic acid*,  $\text{HNbO}_4 + n\text{H}_2\text{O}$ , is obtained by warming niobic acid with hydrogen peroxide on the water-bath; the conversion is not, however, complete, and the acid is more easily prepared by treating its potassium salt with dilute sulphuric acid and subjecting the mixture to dialysis. The dialysed solution is evaporated on the water-bath when the perniobic acid is obtained as a gelatinous precipitate which dries to a yellow, amorphous powder insoluble in water; it is not decomposed by dilute sulphuric acid at the ordinary temperature, but decomposes on heating, with formation of hydrogen peroxide; concentrated sulphuric acid decomposes it with evolution of ozone and oxygen, and when heated at  $100^{\circ}$  it gradually decomposes with evolution of oxygen. The *potassium salt*,  $\text{K}_4\text{Nb}_2\text{O}_{11} + 3\text{H}_2\text{O}$ , is obtained by fusing niobium pentoxide (1 mol.) with potassium hydroxide (8 mols.) in a silver crucible, the product is extracted with the least possible amount of water and the filtrate warmed with a small quantity of hydrogen peroxide, filtered, and precipitated with alcohol; the amorphous precipitate is washed with alcohol and ether, dissolved in a solution of hydrogen peroxide and potassium hydroxide, and again precipitated with alcohol; it is a white, crystalline powder, soluble in water, evolves oxygen when warmed, and hydrogen peroxide or ozonised oxygen when treated with dilute or concentrated sulphuric acid. Of the 11 atoms of oxygen, 4 atoms are active, so that the salt is a compound of pyroperniobic acid with 2 mols. of potassium peroxide and 2 mols. of potassium oxide. When allowed to remain in aqueous solution, it is slowly decomposed into the salt,  $\text{KNbO}_4$ , together with acid salts of the pyro-acid.

*Pertantallic acid*,  $\text{HTaO}_5 + n\text{H}_2\text{O}$ , is obtained as a white, powdery precipitate by treating its potassium salt with dilute sulphuric acid. It has similar properties to perniobic acid, but is more stable and is not decomposed by heating at  $100^{\circ}$ . The *potassium salt*,  $\text{K}_3\text{TaO}_8 + \frac{1}{2}\text{H}_2\text{O}$ , is obtained by fusing tantalum pentoxide with potassium hydroxide and treating the melt in a similar way to that described for the salt of perniobic acid; it has similar properties to the perniobate, and since it contains four active oxygen atoms is a salt of orthopertantallic acid in which the hydrogen atoms are replaced by the radicle KO. The *barium salt* is obtained as a white, voluminous precipitate when barium chloride is added to the aqueous solution, and is decomposed by carbonic anhydride with formation of hydrogen peroxide.

*Potassium calcium pertantalate*,  $\text{KCaTaO}_8 + 4\frac{1}{2}\text{H}_2\text{O}$ , is obtained as a fine, crystalline powder by adding calcium chloride to a solution of

the potassium salt; it forms microscopic, rhombic prisms, is insoluble in cold water, and when warmed with water forms a voluminous precipitate, the solution becoming alkaline, and oxygen being evolved. The *sodium* salt,  $\text{Na}_3\text{TaO}_8 + \text{H}_2\text{O}$ , is obtained by warming sodium hexatantalate with hydrogen peroxide and adding sodium hydroxide; the filtered solution is treated with excess of hydrogen peroxide, cooled with ice, and precipitated with alcohol. It is a white, amorphous powder, difficult to dissolve in water.

The *sodium* salt,  $\text{NaTaO}_4 + \text{NaO} \cdot \text{TaO}_4 + 13\text{H}_2\text{O}$ , is obtained by evaporating a solution of sodium hexatantalate to dryness on the water-bath; the aqueous extract of the residue is treated with a few drops of hydrogen peroxide and precipitated with alcohol. It is a white, amorphous powder, and yields hydrogen peroxide when treated with dilute sulphuric acid.

The examination of pervanadic, pernibic, and pertantallic acids shows that their salts are less stable as the atomic weight of the metal from which they are produced decreases (Abstr., 1898, ii, 165 and 337).  
E. C. R.

**Preparation of Potassium Platosochloride.** By MAURICE VÈZES (*Bull. Soc. Chim.*, 1898, [iii], 19, 879—883).—The treatment of potassium platinochloride with a quantity of normal potassium oxalate sufficient to effect the reduction of the salt without converting it into platoso-oxalate (see this vol., i, 572) constitutes a simple and economical means of preparing potassium platosochloride. For this purpose, 100 grams of the platinochloride and 37 grams of potassium oxalate are boiled with a litre of water for several hours until all is dissolved; on cooling the solution, potassium platosochloride crystallises out to the extent of about 80 per cent. of the theoretical yield, and a further quantity is precipitated by adding alcohol to the mother liquor.  
N. L.

**Volatilisation of Osmium in a Current of Air or Oxygen.** By MAURICE VÈZES (*Zeit. anorg. Chim.*, 1899, 20, 230—232).—The author points out that Šulc's observations (this vol., ii, 299) on the oxidation and subsequent volatilisation of osmium are not new. The amount of oxidation, and subsequent loss in weight, depends on the physical condition of the osmium, that is, on the fineness of the powder and the method by which it is prepared.  
E. C. R.

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### Mineralogical Chemistry.

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Sulphur and other Minerals from the Malfidano Mines near Buggerru, Sardinia. By FEDERICO MILLOSEVICH (*Real. Accad. dei Linc.*, 1898, 7, 249—254).—Measurements are given of crystals of sulphur and anglesite obtained from galena. The sulphur crystals are very small, being never more than 1·5 mm. in longest diameter ; they are,

however, very rich in brilliant faces, in one case 27 different forms occurring on a single crystal. Three new forms are observed, namely, (305), (155), and (319), bringing the total number of forms known up to 36. The axial ratios observed were  $[a:b:c=0.81368:1:1.90472]$ , whilst von Kokscharoff obtained  $[a:b:c=0.81309:1:1.90339]$ . The anglesite crystals, which are colourless and transparent and attain a length of 5 mm., do not exhibit new forms; they give the axial ratios  $[a:b:c=0.78547:1:1.28877]$ , von Kokscharoff's numbers being  $[a:b:c=0.78516:1:1.28939]$ . T. H. P.

**Hungarian Coals, &c.** By ALEXANDER VON KALECSINSZKY (*Jahresber. k. ung. geol. Anstalt*, 1897 (for 1894) 162—170; 1898 (for 1896), 198—203. Compare Abstr., 1897, ii, 417).—Technical analyses are given of coals, clays and petroleum. L. J. S.

**Analyses of Austrian Minerals, &c.** By CONRAD H. VON JOHN and C. FRIEDRICH EICHLEITER (*Jahrb. k. k. geol. Reichsanstalt, Wien*, 1898 (1897), 47, 737—766. Compare Abstr., 1896, ii, 252).—This is a collection of numerous (203) technical analyses of coals, ores, waters, rocks, salts, petroleum, artificial products, &c., made during 1895—7 in the Chemical Laboratory of the Royal Geological Institute at Vienna.

Graphite from St. Lorenzen, Styria, gave I; from Březinec near Gewitsch, Moravia, II:

	C.	Ash.	Hygroscopic H <sub>2</sub> O.	Comb. H <sub>2</sub> O.	Total.
I.	66.22	30.55	1.60	1.63	100.00
II.	7.40	84.20	8.35		99.95

Fahlerz from Payerbach gave: Cu, 31.15; Ag, 0.024; Au, 0.001 per cent., also S, Sb, Zn, and Pb.

Decomposed wollastonite from near Üsküb gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	Loss on ignition.	Total.
43.36	7.82	5.04	39.70	2.56	2.06	100.54

L. J. S.

**Goldschmidtite, a New Mineral.** By WILLIAM H. HOBBS (*Amer. J. Sci.*, 1899, [iv], 7, 357—364).—The new mineral was found as small, bright, prismatic crystals on chalcedony in a granite-breccia cemented by phonolite from the Gold Dollar mine in Arequa Gulch, Cripple Creek district, Colorado. The symmetry is monoclinic, and possibly clinohedral, with  $[a:b:c=1.8562:1:1.2981; \beta=89^\circ 11']$ ; a list of 22 forms is given. The colour is silver-white with bright metallic lustre; streak dull greyish-black. Brittle; H=2. There is a perfect cleavage parallel to  $b(010)$ , and the crystals are frequently twinned on  $a(100)$ . Analysis made on about 0.1 gram of nearly pure material gave the formula  $\text{Au}_2\text{AgTe}_6$ .

Au.	Ag.	Te.	Total.
31.41	8.95	[59.64]	100.00

This composition is intermediate between that of sylvanite,  $\text{AuAgTe}_4$ , and of calaverite,  $(\text{Au,Ag})\text{Te}_2$ , and it is suggested that the three minerals form a homologous series, as in the humite-group; in passing

from calaverite to sylvanite, there is a gain of  $\text{Ag}_2\text{Te}$  and a loss of  $\text{Au}_3^5$ .

Calaverite.....  $\text{Au}_{\frac{2}{3}}^7\text{Ag}_{\frac{1}{3}}^5\text{Te}_{21}$

Goldschmidtite.....  $\text{Au}_{\frac{2}{3}}^2\text{Ag}_{\frac{1}{3}}^{11}\text{Te}_{22}$

Sylvanite .....  $\text{Au}_{\frac{1}{3}}^{17}\text{Ag}_{\frac{1}{3}}^7\text{Te}_{23}$

Between goldschmidtite and sylvanite there is a somewhat close crystallographic relationship; for sylvanite  $[a:b:c = 1.6339:1:1.1265; \beta = 89^\circ 35']$ , and the cleavage is also  $b(010)$ . L. J. S.

**Minerals Associated with Diamonds from Bahia.** By EUGEN HUSSAK (*Tsch. Min. Mitth.*, 1899, 18, 342—359).—A description is given of 39 minerals occurring in the diamond sands of Bahia, Brazil.

Diaspore in cleavage flakes, closely resembling the accompanying kyanite in appearance, gave, on analysis,  $\text{Al}_2\text{O}_3$ , 85.48, loss on ignition, 15.01 = 100.49.

Ilmenite (hydroilmenite) occurs as rounded grains, often with a nut-brown crust of an earthy decomposition product. The latter also occurs as rolled grains with bright cleavages following the parting planes of the original ilmenite, and in places enclosing specks of ilmenite and minute needles of rutile; analysis gave  $\text{TiO}_2$ , 65.50; loss on ignition, 4.94, the remainder being only iron. The alteration of ilmenite therefore consists of the separation of the iron as ferric oxide, and the titanate as rutile or anatase. L. J. S.

**Occurrence, Origin and Composition of Chromite.** By JULIUS H. PRATT (*Amer. J. Sci.*, 1899, [iv], 7, 281—286).—Chromite occurs in the peridotites of North Carolina as scattered grains or crystals, but near the margins of the intrusive masses it is more abundant and fills large pockets. Like the corundum (*Abstr.*, 1898, ii, 603) in the same rocks, the chromite has been one of the first minerals to crystallise out from the magma. The magma may be regarded as a solution from which the more basic minerals (chromite, spinel and corundum) are the first to crystallise, not according to their fusibility, but according to their solubility in the fused mass. There would, therefore, be a concentration of these minerals at the cooling margins of the intrusive mass.

The following analyses by C. Baskerville and H. W. Foote, are given of pure selected chromite from: I, Price's Creek in Yancey Co.; II, Corundum Hill in Macon Co.; III, Webster in Jackson Co.

	$\text{Cr}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{FeO}$	$\text{MgO}$	$\text{SiO}_2$	$\text{MnO}$	Formula.
I.	59.20	7.15	25.02	4.42	3.20	0.92	10 Ch. + 2 Sp. + $\text{MgO}, \text{Cr}_2\text{O}_3$ .
II.	57.80	7.82	25.68	5.22	2.80	0.69	9 Ch. + 2 Sp. + $\text{MgO}, \text{Cr}_2\text{O}_3$ .
III.	39.95	29.28	13.90	17.31	—	—	Ch. + 2 Sp. + $\text{MgO}, \text{Cr}_2\text{O}_3$ .

Ferric oxide was shown to be present, but the amount could not be determined, so that the bivalent oxides in the analyses are slightly in excess of the trivalent. In the formulæ given above, Ch. (chromite) =  $\text{FeO}, \text{Cr}_2\text{O}_3$ , and Sp. (spinel) =  $\text{MgO}, \text{Al}_2\text{O}_3$ ; the third isomorphous molecule,  $\text{MgO}, \text{Cr}_2\text{O}_3$ , is not known as a natural mineral. Analyses I and II represent the composition of the majority of chromites; only

two terrestrial occurrences being known which are pure  $\text{FeO}, \text{Cr}_2\text{O}_3$ . An increase in the amount of alumina and magnesia gives a passage to picotite (chrome-spinel); for intermediate members having a composition similar to that shown by analysis III, the new name *mittellite* is proposed. This mineral from Webster differs from ordinary chromite in being much coarser grained; it appears to be identical with Bock's magnochromite from Silesia (Abstr., 1874, 666). L. J. S.

**Barytocelestines.** By C. W. VOLNEY (*J. Amer. Chem. Soc.*, 1899, 21, 386—388).—A new barytocelestine from the Silurian limestones of Eastern Ontario is described. It has the composition  $\text{BaSO}_4, 3\text{SrSO}_4$ , and contains traces of ferric oxide and alumina. Its specific gravity is 4.123. T. H. P.

**New Cobaltiferous and Nickeliferous Minerals from Messina.** By GIUSEPPE LA VALLE (*Real. Accad. dei Linc.*, 1898, 7, 68—71).—In the dolomitic limestone from the territory of Mandanici near the Peloritani mountain range, there are conglomerates of limonite, malachite, and azurite mixed with a yellow, ochreous, earthy substance, which are more or less friable. On breaking these masses, the surfaces of fracture are in some cases covered with a crimson layer, which, under the microscope, is seen to have a fibrous structure, and to consist of small crystals with a pearly or vitreous lustre. These crystals are apparently monoclinic, the angle  $(100) : (001)$  being about  $54^\circ$ ; they colour a borax bead sapphire blue, and from this, they are considered to be crystals of erythrite. Scattered here and there in the earthy mass mentioned above, flaky globules are also found of a beautiful, apple-green colour and a light indigo-blue coating. On chemical examination, the globules prove to be annabergite, possibly derived from the decomposition of cobaltiferous and nickeliferous pyrites. The blue substance, which contains arsenic and iron, the author regards as symplectite,  $\text{Fe}_3\text{As}_2\text{O}_8 + \text{Aq}$ . Along with the above-described minerals, there occurs also a brown substance in the form of minute granules or amorphous globules; this contains cobalt and manganese, and is probably asbolan.

Such associations of minerals have also been found in other parts of Sicily. T. H. P.

**Powellite Crystals from Michigan.** By CHARLES PALACHE (*Amer. J. Sci.*, 1899, [iv], 7, 367—369).—Powellite was first discovered in Idaho (Abstr., 1891, 886) and afterwards at the South Hecla Copper Mine, Houghton Co., Michigan (Abstr., 1894, ii, 240). A crystallographic description is given of two fine crystals from the latter locality; these show the symmetry of scheelite (tetragonal, pyramidal-hemihedral), with angles closely agreeing with Melville's determinations for the original powellite. The colour is pale bluish-green, and the sp. gr. 4.355. A third specimen, consisting of a rounded mass of powellite, has the same bluish-green colour in the central part, shading off in the surface layer to black and opaque, or in thin splinters deep Prussian-blue. The dark coloured portion has the lower sp. gr. of 4.214; it is therefore probably almost pure calcium molybdate (calculated sp. gr. 4.267) with very little calcium tungstate.

L. J. S.

**Solubility of Natural Silicates in Water.** By GEORGE STEIGER (*J. Amer. Chem. Soc.*, 1899, 21, 437—439).—In extension of Clarke's qualitative experiments on the alkaline reaction of natural silicates, the amount of alkali dissolved by a given volume of cold water acting for a definite time on a number of natural silicates has been determined.

T. H. P.

**Roscoelite.** By WILLIAM F. HILLEBRAND, HENRY W. TURNER and FRANK W. CLARKE (*Amer. J. Sci.*, 1899, [iv], 7, 451—458).—The analyses of Roscoe and Genth of this rare vanadium mica are not in agreement; a new analysis has therefore been made with carefully purified material from the Stockslager mine on Granite Creek in Eldorado Co., California. By heating the mineral with dilute sulphuric acid in an atmosphere of carbonic anhydride in sealed tubes, and titrating, it was found that 93·5 per cent. of the vanadium existed as  $V_2O_3$ . Allowing for slight oxidation, it is therefore assumed, with Genth, that the whole of the vanadium exists as  $V_2O_3$  rather than as  $V_2O_5$ , as given by Roscoe. The results of the new analysis are:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	V <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.
45·17	0·78	24·01	11·54	1·60	1·64	10·37	0·06
	Li <sub>2</sub> O.	H <sub>2</sub> O 105°.	H <sub>2</sub> O 280°.	H <sub>2</sub> O > 280°.		Total.	
	trace	0·40	0·17	4·12		99·86	

Neglecting titanic oxide and water lost below 280°, the above composition may be approximately expressed by Clarke's mica theory (*Abstr.*, 1897, ii, 52) as  $Al(SiO_4)_3FeKMg_2H_2 + Al(Si_3O_8)_3AlK_2H_4 + 8Al(SiO_4)_3V_2KH_2$ . The first of these molecules represents the normal phlogopite type, the second is a trisilicate alkaline biotite, and the third a muscovite with two-thirds of the aluminium replaced by vanadium. Roscoelite may therefore be considered to be essentially a vanadium muscovite.

Roscoelite has been found in association with gold at four localities in Eldorado Co., California. It occurs at the junction of intrusive granodiorite with the surrounding sediments and lavas. The mineral is optically negative and biaxial, with a very small angle, being almost uniaxial; it is pleochroic.

L. J. S.

**Hydromica from New Jersey.** By FRANK W. CLARKE and NELSON H. DARTON (*Amer. J. Sci.*, 1899, [iv], 7, 365—366).—The walls of calcite veins in a decomposed diabase at Rocky Hill, New Jersey, are lined with a thin coating of a bronze-yellow hydromica, which in places also extends down the cleavage planes into the masses of calcite. The mineral is soft and is composed of minute flakes thinly matted together. It is optically biaxial with a very small angle, and is pleochroic. Before the blowpipe, it fuses without exfoliation to a dark-coloured bead; it is readily decomposed by hydrochloric acid. Analysis by G. Steiger gave, after deducting 18·5 per cent. of calcite and a little titanic oxide,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	K <sub>2</sub> O, Na <sub>2</sub> O.	H <sub>2</sub> O 100°.	H <sub>2</sub> O > 100°.	Total.
40·24	10·34	24·57	5·21	6·78	2·20	3·03	7·63	100·00

This gives, according to Clarke's mica theory (*Abstr.*, 1897, ii, 52), the formula,  $3Al(SiO_4)_3Al_2KH_2 + 6R'''(SiO_4)_3H_3R'''_2 + 5R'''(SiO_4)_3R'''_3H_2$

+ 3H<sub>2</sub>O, where R''' = Al : Fe''' :: 2 : 3 and R'' = Fe'' : Mg :: 3 : 7. The muscovitic and phlogopitic molecules are in the ratio of 9 : 5. Since the potassium is largely replaced by water, and there is water of crystallisation, the substance is a mica altered to vermiculite. The large amount of ferric oxide is unusual (compare baddeckite, this vol., ii, 110), and suggests that the original mineral was a ferric muscovite, a mineral which is theoretically possible, although not known.  
L. J. S.

**Chloritoid from Hungary.** By JULIUS SZÁDECZKY (*Sitz.-Ber. Siebenbürg. Museumvereins*, 1897 (1896), 19, *Revue*, 1—8).—The phyllites of the Zsil Valley near Surduk, in the Southern Carpathians (Comitat Hunyad) contain crystals of chloritoid, which on analysis by Béla Ruzitska gave the following results. The material analysed was much intergrown with quartz and hæmatite :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O.	Total.
33·20	37·91	7·50	18·79	1·03	1·90	100·33

The material is only slightly soluble in concentrated hydrochloric acid, but is completely decomposed with separation of silica by long boiling in concentrated sulphuric acid.  
L. J. S.

**Scottish Silicates.** By M. FORSTER HEDDLE (*Trans. Roy. Soc. Edin.*, 1899, 39, 341—359).—Nineteen analyses are given of silicates to which the old name schorl was formerly indiscriminately applied.

I. Tourmaline, as jet-black crystals from a granite vein near Struay Inn, Ross-shire ; contains also F 1·71, P<sub>2</sub>O<sub>5</sub> trace, and by difference, B<sub>2</sub>O<sub>3</sub> 10·77 per cent.

II. Fibrolite, as fibres surrounding, and in parallel growth with, red andalusite from Clashnaree Hill, near Auchendoir, Aberdeenshire.

III. Kyanite from North Glen Esk, Forfarshire. IV. Kyanite as blue crystals in margarodite-slate from Glen Urquhart, Inverness-shire.

V. Epidote as olive-green crystals embedded in hornblende from Nudista, Hillswick, Shetlands. VI. Epidote, pale-green crystals embedded in prehnite from Delnabo, Glen Gairn, Aberdeenshire.

VII. Zoisite in quartz from Milltown, Glen Urquhart. VIII. Zoisite as large, grey crystals from the same locality. IX. Zoisite as grey crystals from Loch Garve, Ross-shire.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp.gr.
I.	35·54	35·55	0·18	7·12	0·31	1·11	3·54	1·07	0·43	2·95	—	—
II.	38·41	61·43	0·21	—	0·11	—	—	—	—	0·23	100·39	—
III.	36·38	58·30	1·61	1·12	—	0·86	—	0·25	0·42	1·45	100·39	3·538
IV.	37·53	58·10	2·09	—	—	0·13	0·08	0·25	0·74	1·20	100·12	3·016
V.	37·87	24·72	9·96	0·36	0·54	23·10	0·77	—	—	2·82	100·14	3·396
VI.	38·37	26·09	10·39	—	0·74	21·65	0·24	—	—	2·44	99·92	—
VII.	41·56	29·90	—	3·21	—	22·14	0·33	0·35	0·68	2·19	100·36	3·014
VIII.	39·51	30·83	—	2·52	0·08	22·81	—	0·68	0·9	2·51	99·83	3·32
IX.	40·07	30·83	1·58	0·48	0·22	23·66	0·48	0·50	0·43	2·10	100·35	3·268

Other (previously published) analyses are given of andalusite, fibrolite, kyanite, epidote, withamite, zoisite, and idocrase.

L. J. S.

**Anatase and Brookite from near Dublin.** By JOSEPH P. O'REILLY (*Sci. Proc. Roy. Dublin Soc.*, 1898, N.S., 8, 732—740).—The heavy residue obtained from a yellowish clay filling joints in the



quartzite at Shankill, near Dublin, was found to contain crystals of quartz and brookite together with tetragonal pyramids resembling anatase in appearance. The last has a sp. gr. 3·578, which is lower than that of pure anatase (3·9); analyses by W. L. Warren of the [homogeneous?] crystals gave I and II; these approximate to Eakin's analysis of "xanthitane," an earthy decomposition of sphene, from North Carolina. It is assumed that the alumina is an essential constituent replacing titanic oxide. The yellowish clay in which the crystals are found gave the results under III.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	MnO	TiO <sub>2</sub>	Alkalis	H <sub>2</sub> O	Total
I.	3·30	12·86	15·20	1·05	2·29	4·42	trace	60·72	0·06	0·06	99·96
II.	3·07	13·02	10·40	6·01	2·16	4·42	trace	60·81	0·12	—	100·01
III.	44·40	35·45	—	6·75	0·65	0·99	—	6·22	0·10	5·46	100·02

The brookite occurs as small, light-brown plates of sp. gr. 3·928.

L. J. S.

**Ores and Rocks from British Columbia.** By J. C. GILLIM and W. S. JOHNSON (*Canadian Record Sci.*, 1897, 7, 293—302).—A description is given of the Southern Slokan Mining Division in West Kootenay, British Columbia. The country rock is a grey granite with quartz, feldspar, biotite and hornblende, and a good deal of accessory sphene. Large crystals of impure orthoclase, enclosing scales of biotite, gave on analysis the results under I. The granite itself gave II.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Total
I.	59·86	20·26	2·90	0·78	12·39	5·76	—	101·95
II.	60·09	17·20	6·73	8·24	0·47	6·23	2·45	101·41

Other rock analyses are given in the paper.

L. J. S.

**Rock-forming Biotites and Amphiboles.** By HENRY W. TURNER, with analyses by WILLIAM F. HILLEBRAND, HENRY N. STOKES and WILLIAM VALENTINE (*Amer. J. Sci.*, 1899, [iv], 7, 294—298).—The following analyses are given of material separated by means of heavy solutions out of rocks from the Sierra Nevada. The powders analysed were examined microscopically, and the small amounts of impurities noted in each case.

I. Black biotite from biotite-granite, at the base of El Capitan, in Yosemite Valley; the phosphoric acid is due to the presence of apatite. The biotite-granite gave analysis II; it contains quartz > plagioclase > orthoclase > biotite, with accessory magnetite, sphene, apatite and zircon.

III. Black biotite in quartz-monzonite, from Blood's Station, Alpine Co. Hillebrand found in the biotite 0·066 and in the rock 0·012 per cent. V<sub>2</sub>O<sub>5</sub>.

IV. Reddish-brown biotite from pyroxenic gneiss, from the North Mokelumne River in the Big Trees quadrangle. Hillebrand found in the biotite 0·127 and in the gneiss 0·08 per cent. V<sub>2</sub>O<sub>5</sub>.

V. Biotite, sp. gr. 3·05, from a block of quartz-monzonite by the Tioga road, south-east of Mt. Hoffmann, in the Mt. Dana quadrangle.

VI. Amphibole, with strong pleochroism (brown to greenish-brown)

and large extinction angle, from amphibole-gabbro, from Beaver Creek, in the Big Trees quadrangle. The amphibole-gabbro (anal. VII, also  $\text{FeS}_2$ , 0.20) is composed chiefly of labradorite and hornblende, with a little pyrites and pyrrhotite.

VIII. Amphibole, sp. gr. 3.203, with large extinction angle and pleochroism in dark green tints, from the same block of quartz-monzonite as No. V. Analysis IX gives the composition of an average quartz-monzonite of the region.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
$\text{SiO}_2$ .....	35.64	71.08	35.62	36.62	35.75	46.08	47.27	47.49	66.83
$\text{TiO}_2$ .....	1.12	0.22	2.61	3.03	3.16	0.77	0.92	1.21	0.54
$\text{ZrO}_2$ .....	—	0.08	—	—	Nil	—	—	Nil	0.04
$\text{Al}_2\text{O}_3$ .....	18.62	15.90	15.24	14.37	14.70	10.56	20.82	7.07	15.24
$\text{Cr}_2\text{O}_3$ .....	—	—	—	—	trace	—	trace	—	—
$\text{V}_2\text{O}_5$ .....	—	—	—	—	0.05	—	0.02	0.04	—
$\text{Fe}_2\text{O}_3$ .....	5.54	0.62	4.69	4.04	4.65	2.81	1.85	4.88	2.73
$\text{FeO}$ .....	14.60	1.31	13.67	17.09	14.08	8.30	4.26	10.69	1.66
$\text{MnO}$ .....	0.79	0.15	0.74	0.40	0.45	0.15	trace	0.51	0.10
$\text{NiO,CoO}$ .....	—	—	—	—	0.02	—	Nil	0.02	—
$\text{CaO}$ .....	0.90	2.60	0.95	1.48	0.17	12.64	13.02	11.92	3.59
$\text{SrO}$ .....	Nil	0.02	trace	trace	?	Nil	trace	Nil	0.03
$\text{BaO}$ .....	trace	0.04	0.26	0.33	0.12	Nil	Nil	Nil	0.11
$\text{MgO}$ .....	9.72	0.54	12.70	9.68	12.37	14.40	6.44	13.06	1.63
$\text{K}_2\text{O}$ .....	9.22	4.08	7.72	8.20	9.19	0.34	0.22	0.49	4.46
$\text{Na}_2\text{O}$ .....	0.38	3.54	0.50	0.45	0.32	1.62	2.75	0.75	3.10
$\text{Li}_2\text{O}$ .....	trace	trace	trace	trace		Nil	Nil	trace	trace
$\text{H}_2\text{O}$ , 110° ..	0.48	Nil	0.94	0.90	1.03	0.17	0.08	—	Nil
$\text{H}_2\text{O}$ > 110° ..	2.54	0.30	4.36	3.26	3.64	1.97	1.27	1.86	0.56
$\text{P}_2\text{O}_5$ .....	0.20	0.10	Nil	Nil	0.03	0.18	0.74	Nil	0.18
$\text{SO}_3$ .....	—	Nil	—	—	—	—	—	—	Nil
$\text{Cl}$ .....	—	0.02	—	—	—	—	trace	—	0.02
$\text{F}$ .....	0.26	—	Nil	0.10	0.17	Nil	—	0.06	—
Total...	100.01	100.60	100.00	99.95	99.90	99.99	99.86	100.05	100.82

II and IX also contained traces of  $\text{CO}_2$ ; in V the water was estimated at 105°.

L. J. S.

**Origin of Palæotrochis** [Analysis of Rhyolite]. By JOSEPH S. DILLER (*Amer. J. Sci.*, 1899, [iv], 7, 337—342).—The name palæotrochis was given by E. Emmons in 1856 to regularly striated bi-conical objects which he regarded as siliceous corals, and the oldest representatives of animal life upon the globe; they occur, together with various shaped concretions, in the so-called Taconic rocks of Montgomery Co., North Carolina. These rocks were formerly considered to be sedimentary quartzites, but it has since been proved that they are volcanic rhyolites. Various authors have previously considered that palæotrochis is merely concretionary, and it is now shown by detailed microscopical examination that these forms are connected with the numerous spherulitic growths in the rhyolite. Similar objects are described from Mexico and Japan.

Analysis by W. F. Hillebrand of the palæotrochis-bearing rock gave :

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO, SrO.	BaO.
79.57	0.11	11.41	0.20	0.70	0.21	0.05
	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.		
	3.52	3.46	0.79	100.02		

The alumina includes a little phosphoric acid, and there is a trace of magnesia present. L. J. S.

**Rocks and Graphite from Ceylon.** By MAX DIERSCHKE (*Jahrb. k.k. geol. Reichsanstalt, Wien*, 1898, 48, 230—288).—A petrographical description is given of a collection of rocks from Ceylon. Graphite and its mode of occurrence at Ragedara are also described. Enclosed in the graphite are quartz, pyrites, apatite, mica, calcite, green orthoclase, and rock fragments. The green orthoclase, sp. gr. 2.621, gave the following results on analysis; the green colour is seen in microscope sections to be due to a chloritic substance :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.
61.88	18.16	0.85	1.64	0.43	0.08	13.82	2.02	99.44

L. J. S.

[**Rock Analyses.**] By FRIEDRICH BECKE (*Tsch. Min. Mitth.*, 1898, 18, 94).—Analysis I, by Mrha, of leucite-basanite from the 1891—1893 lava-flow at Atrio del Cavallo, Vesuvius; II, by H. Krczmař, of tonalite-gneiss, from Wistra, Carinthia.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	Loss on ignition.	Total.
I. 48.99	19.82	2.59	5.26	8.13	2.82	9.06	3.17	0.33	—	100.17
II. 63.09	18.89	3.48	2.02	6.18	1.97	1.30	3.14	—	0.63	100.70

L. J. S.

[**Classification of the Volcanic Rocks of Mont-Dore.**] By MICHEL LÉVY (*Compt. rend.*, 1899, 128, 1078—1082).—The volcanic rocks of Mont-Dore are divisible into two series, a central and a peripheral one. The rocks composing these series originate from two different foci of volcanic activity, and analysis shows that there is a corresponding difference in their petrographical and chemical characters. Rock specimens from the central series have already been analysed; those from the peripheral group have only recently been studied by Bonjean (see following abstract). The magma of the peripheral rocks is very rich in alkalis, potash and soda being present in nearly equal proportions; they contain but little lime. The rocks of the central series consist of basic andesite, labradorite, basalt, and trachyte; these contain more soda than potash, and more lime is present than in the peripheral series. The rocks of both series contain notable quantities of magnesia and ferric oxide. G. T. M.

**Analyses of Volcanic Rocks from the Peripheral Series of Mont-Dore.** By EDMOND BONJEAN (*Compt. rend.*, 1899, 128, 1096—1097).—Eleven analyses of volcanic rocks from the peripheral series of Mont-Dore; the specimens analysed belong to the following

petrographical species : phonolites, trachytes, tephrite with hainyue, and compact and ophitic basalts (see preceding abstract). G. T. M.

**Association of Argillaceous Rocks with Quartz Veins in Brazil.** By ORVILLE A. DERBY (*Amer. J. Sci.*, 1899, [iv], 7, 343—356).—In the diamond mining region of Diamantina, Minas Geraes, argillaceous selvages are frequently associated with the quartz veins of the metamorphic series. The most frequent is a reddish, foliated clay, which has resulted from the decomposition of a micaceous schist. The inner portions of the veins contain nests of white kaolin mixed with quartz ; this has probably been derived from a pegmatite injected in the micaceous schist. A pure sample of the granular kaolin, on analysis by E. Hussak, gave  $\text{SiO}_2$ , 44.96 ;  $\text{Al}_2\text{O}_3$ , 42.09 ;  $\text{H}_2\text{O}$ , 13.25 per cent. A detailed account is given of these clays and the rocks of the district, and in discussing the relations between them the indications of the heavy residues (containing rutile, anatase, xenotime, monazite, &c.) are made use of. An analysis by Hillebrand is given of kyanitic schist. L. J. S.

**Tachylite from the Floor of the North Atlantic.** By PIERRE TERMIER (*Compt. rend.*, 1899, 128, 1256—1258. Compare this vol., ii, 436).—The fragments of tachylite or hyalobasalt, dredged in the North Atlantic at a point 500 miles to the north of the Azores, contain small, idiomorphic crystals of translucent olivine, together with a series of polychroic, doubly refractive dark brown stains intermingled with a network of fine trichites, all embedded in a vitreous matrix. The stains and trichites appear to indicate an incipient crystallisation of some mineral species, the optical characters of the stains corresponding with those of a ferruginous hornblende. The appearance of this mineral, however, to the exclusion of augite, would be somewhat remarkable, and, moreover, the refractive index of the stains differs only slightly from that of the matrix. G. T. M.

**Alleged Existence of Fluorine in certain Mineral Waters.** By F. PARMENTIER (*Compt. rend.*, 1899, 128, 1100—1101).—Specimens of glass subjected for some time to the action of the waters of Mont-Dore and Saint-Honore-les-Bains become covered with opaque stains resembling those produced by hydrofluoric acid ; these stains are due, however, to the deposition of silica and calcium carbonate. They may be removed by scraping the glass with a sharp knife, and the original lustre of the glass is restored on dipping it in dilute hydrofluoric acid. Moreover, numerous analyses have failed to reveal the presence of fluorine in these mineral waters. G. T. M.

**Mineral Waters from East Bohemia.** By CONRAD H. VON JOHN (*Jahrb. k.k. geol. Reichsanstalt, Wien*, 1898, 48, 375—388).—Detailed analyses are given of seven waters from East Bohemia. The composition is not that of normal spring water ; the predominating sulphates probably owe their origin to the decomposition of pyrites in the rocks from which the waters issue. L. J. S.

**Chemical Investigations in the Red Sea.** By KONRAD NATTERER (*Monatsh.*, 1899, 20, 1—263).—A detailed account is given

of the chemical researches made during a voyage on board the *Pola*, extending from October, 1895, to May, 1896. A large number of analyses were made of the water and of the sea-bottom of the northern half of the Red Sea, and of the Gulfs of Suez and Akaba. Investigations were also made as to the character of the surrounding coasts and of the islands of these waters. Relations are traced between the results obtained and the configuration and movements of the water.

The paper is accompanied by numerous tables of analytical numbers and by maps showing the positions of the stations where observations were made, the depth of water, &c.

T. H. P.

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## Physiological Chemistry.

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**A Relation between Intra-organic Oxidations and the Production of Kinetic Energy in the Organism.** By ALEXANDRE POEHL (*Compt. rend.*, 1899, 128, 1046—1047).—The author has previously shown that certain mineral waters have a very high osmotic pressure, and their ingestion causes a notable increase in the osmotic pressure of the urine as measured by the reduction in its freezing point. He now finds that the administration of spermine hydrochloride in sodium chloride solution likewise causes an increase in the osmotic pressure of the urine, accompanied by a remarkable increase in the proportion of chlorides and by a high coefficient of intraorganic oxidation. The breaking-down of proteids into substances of lower molecular weight necessarily increases the osmotic pressure of the liquids containing them, and the increase in osmotic pressure produced by spermine confirms the author's view that the physiological effect of this substance is due to a power of accelerating intra-organic oxidation. C. H. B.

**Reducing Power of Tissues: the Blood.** By HENRI HÉLIER (*Compt. rend.*, 1899, 128, 1043—1046. Compare this vol., ii, 374).—The blood has very considerable reducing power, and with the exception of the lymph exceeds in this respect every other tissue of the animal body. As a rule, the venous blood has more reducing power than arterial blood, but this is not always the case, and the difference seems to be due, in part at least, to the variable distribution of the blood corpuscles. After food, the number of corpuscles increases in venous blood, but diminishes in arterial blood. The reducing power of the blood increases rapidly as the blood becomes charged with the products of digestion, and then diminishes slowly as nourishment is provided to the other tissues.

The reducing power of the blood varies under the influence of many other causes, such as variable distribution of the corpuscles, variations in the quantity of plasma, and variations due to elimination of the reducing substances resulting from want of assimilation. C. H. B.

**Similarity of the Absorption of Liquids in Muscles and in Soaps.** By JACQUES LOEB (*Pflüger's Archiv*, 1899, 75, 303—309).—In a 0·7 per cent. solution of sodium chloride, a muscle takes up only 1 per cent. of water in 18 hours; in an isotonic solution of lithium chloride, its weight remains unchanged. In an isotonic solution of potassium chloride, bromide, or iodide, the muscle takes up 40 per cent. of its weight; in solutions of the chlorides of calcium, strontium, barium, cobalt, or manganese, 20 per cent. This relationship of the absorption of liquids in muscles shows a complete analogy to what occurs in sodium, potassium, or calcium soaps. The main cause in both cases is osmotic pressure, and not capillary force. W. D. H.

**Absorption of Iodine by the Skin, and its Localisation in Certain Organs.** By F. GALLARD (*Compt. rend.*, 1899, 128, 1117—1120).—As the result of experiments made on rabbits, the author draws the following conclusions. 1. The healthy skin is penetrated by aqueous solutions of iodides, and the iodine thus introduced into the system can be recognised and estimated in the urine and viscera. 2. The diet plays an important part in the elimination of the iodine. 3. Certain organs, the brain, for example, absorb relatively large proportions of the element. Only a portion of the animal's abdomen was bathed in the iodide solution, and tables are given showing the relationship between the number of baths and the amount of iodine in the urine. The change from the ordinary vegetable fare to a dry, amylaceous diet produces a marked increase in the amount of iodine eliminated. Those organs, like the brain and glands, which are richest in phosphorus and nuclein compounds have the greatest absorptive power for iodine. G. T. M.

**Fats of Carbonic Oxide in the Animal Body.** By F. WACHHOLTZ (*Pflüger's Archiv*, 1899, 75, 338—340. Compare this vol., ii, 372).—Gaglio (*Arch. exp. Path. Pharm.*, 22, 233) has recently published a paper on this subject, in which the conclusions are in the main different from those of the author. Gaglio's methods are not regarded as trustworthy. W. D. H.

**Behaviour of Glucosamine Hydrochloride in the Animal Body.** By EDMUND FABIAN (*Zeit. physiol. Chem.*, 1899, 27, 167—177).—Glucosamine hydrochloride is not a source of glycogen. It is recognisable in the intestine 12 hours after its administration, and is found in the urine after large doses (15—20 grams), but not after small doses (3 grams). After subcutaneous injection in doses of 2—3 grams, most of it is found in the urine. The experiments were made on rabbits. W. D. H.

**Inorganic Compounds, and Especially those of Iron, in the Human Fœtus.** By LOUIS HUGOUNENQ (*Compt. rend.*, 1899, 128, 1054—1056).—A full developed normal human fœtus contains about 100 grams of inorganic compounds, but the quantity of ferric oxide present is only about 0·42 gram. During the last three months of fœtal life, the absorption of inorganic compounds in general and of iron compounds in particular by the fœtus is twice as great as during

the whole of the preceding six months. This excessive drain of inorganic salts from the mother may account for the malnutrition and other pathologic effects often observed during the later stages of pregnancy, and it would probably be advantageous to give, during this period, a diet unusually rich in iron, phosphorus, and calcium. The administration of compounds of these elements in the form of medicine is, however, of little utility.

C. H. B.

**Lecithin and other 'Myelin Substances' in Brain and Egg-Yolk.** By G. ZUELZER (*Zeit. physiol. Chem.*, 1899, 27, 254—266).—The method adopted for the separation of myelin substances in the brain is as follows: The brain is first extracted with ether. On partial evaporation of the ether, the protagon is partly precipitated; on the removal of this and addition of acetone, a voluminous precipitate is obtained; this is free from cholesterol, which remains in solution. The precipitate consists of several substances containing phosphorus; one of these, protagon, is insoluble in ether free from cholesterol; the part which is soluble in ether is divisible by addition of excess of alcohol into two parts; the one which remains in solution is lecithin, the other, which is precipitated, consists of two new 'myelin substances' which have still to be fully identified. Egg-yolk gives somewhat similar results.

W. D. H.

**Formation of Uric Acid.** By J. WEISS (*Zeit. physiol. Chem.*, 1899, 27, 216—218).—Croton oil irritates the intestine and causes an increase of leucocytes there, but it does not produce an increase of uric acid in the urine. Glycocine and uric acid itself also give negative results. Feeding with thymus or pancreas produces increase of uric acid, which is not prevented by a simultaneous dose of quinic acid.

W. D. H.

**Excretion of Phosphoric Acid after Castration.** By FRIEDRICH N. SCHULZ and O. FALK (*Zeit. physiol. Chem.*, 1897, 27, 250—254).—Curatulo and Tarulli (*Centr. Physiol.*, 1895, 9, 149—152) state that, after castration, animals secrete much less phosphoric acid in their urine; they regard this as due to a retention of the phosphates in the body. The present experiments, made on bitches before and after removal of the ovaries, lend no support to this statement; the amount of urinary phosphate is practically unchanged.

W. D. H.

**Fractional Precipitation of the Products of Peptic Digestion by Zinc Sulphate.** By E. ZUNZ (*Zeit. physiol. Chem.*, 1899, 27, 219—249).—By means of zinc sulphate, the products of gastric digestion can be fractionally precipitated. The characters of each fraction are described, and agree very closely with those previously separated with ammonium sulphate by Pick, but zinc sulphate is stated to be the more convenient reagent. The eight fractions are proto-albumose, hetero-albumose, four varieties of deuto-albumose, and two of peptone.

W. D. H.

**Toxic Action of Sugars.** By JULIUS VON KÓSSA (*Pflüger's Archiv*, 1899, 75, 310—331).—Large doses of sugar injected subcutaneously, or small doses repeated for a long time, produce pathological changes in



the organism. The sugars used in the research were principally cane sugar and dextrose; the animals were birds and mammals; the symptoms observed were cyanosis of the comb (in birds), bronchial catarrh, œdema of lungs, diarrhœa, muscular weakness and sleepiness, incoordination, polydipsia, a gouty state, nephritis, and an increased secretion of total nitrogen, urea, and ammonia in the urine. Special attention is directed to symptoms similar to those seen in diabetes.

W. D. H.

**Action of Tolylenediamine on the Red Corpuscles.** By LOUIS LAPICQUE and A. VAST (*Compt. rend.*, 1899, 128, 1244—1247).—Metatolylenediamine [ $\text{Me}:(\text{NH}_2)_2 = 1:2:4$ ], introduced subcutaneously into dogs, brings about destruction of the red corpuscles, but its action is not entirely direct, for very little hæmoglobin is found dissolved in the blood plasma, although iron accumulates in the liver and spleen. The poison in small doses diminishes the resistance of the blood corpuscles to plasmolysis; this is demonstrated experimentally by placing some of the blood in hypotonic saline solutions of decreasing concentration; it also produces an alteration in the colouring matter consequent on the formation of methæmaglobin; with large doses this change is so pronounced that the blood becomes chocolate coloured. This alteration and weakening of the red corpuscles leads to their destruction by the hæmatolytic organs, and especially the liver.

G. T. M.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Decomposition of Cement by Bacteria.** By ALBERT STUTZER and R. HARTLEB (*Zeit. angew. Chem.*, 1899, 402—403).—The loss of calcium by a cement exposed to the prolonged action of ordinary drinking water is due, not only to the solvent action of carbonic acid, but may also depend to some extent on the action of bacteria. The brownish, muddy residue of a cement which had lain in water for a long time was washed with sterilised water and then added to a solution of ammonium sulphate containing 1 gram per litre. In 6 days, nitrite was found to be present, and in 14 days the ammonia had entirely disappeared. Asparagine is also converted into nitrite, but much more slowly, and sodium nitrite is slowly oxidised to nitrate through the agency of the microbes present in the cement. E. W. W.

**Fermentation of Bilberry Must.** By R. OTTO (*Bied. Centr.*, 1899, 28, 284—286; from *Landw. Jahrb.*, 1898, 261).—Bilberries from Upper Silesia contained acid corresponding with 0.91 to 1.46 per cent. of tartaric acid, and 3.5 to 7 per cent. of sugar. The must which naturally flows from the crushed berries is less acid, and richer in sugar, than that obtained by artificial pressure. To obtain wine which will keep, a considerable amount of sugar has to be added.

Fermentation with ordinary yeast is only vigorous in presence of nitrogenous matter, such as ammonium chloride, or, better, asparagine

(0.6 gram in 1 litre). Pure yeast produced vigorous fermentation in must to which sugar and water alone were added, but the process was  $3\frac{1}{2}$  times as long as when nitrogen compounds were present. The best results were obtained with pure yeast and ammonium chloride (20 to 30 grams per hectolitre).  
N. H. J. M.

**Sterilisation of Potable Waters by Ozone.** By LOUIS MARMIER and HENRI ABRAHAM (*Compt. rend.*, 1899, 128, 1034—1035).—Potable water was treated on a large scale with a current of ozone, conducted from the generator into channels of masonry along which flowed the water to be treated. All the pathogenic organisms are destroyed, and only some germs of *Bacillus subtilis* resist the action of the gas. The reduction in the quantity of dissolved organic matter also makes the water a less favourable nidus for any germs that may subsequently fall into it.  
C. H. B.

**Experiments with Ferric Sulphate for Killing the Denitrifying Organisms of Stable Manure, and for Preventing Erysipelas and Swine Fever.** By O. MÜLLER (*Bied. Centr.*, 1899, 28, 348; from *J. Landw.*, 1898, 207).—The preparation employed contained: ferric sulphate, 66.18, sulphuric anhydride, 6.40, and ferrous sulphate, 5.30 per cent. In the case of pure cultivations of denitrifying organisms, the addition of 1 gram of the powder sufficed to sterilise 10 grams of the slightly alkaline solution, or more of a neutral solution, in 24 hours. It is best to employ a solution for destroying the microbes in fæces; 40 c.c. of a 5 per cent. solution is sufficient for 100 grams of manure.

Experiments with pure cultures of erysipelas and swine fever bacteria showed that they were killed by 0.5 per cent. of the powder.

N. H. J. M.

**Barium in Plants and Soil.** By RICHARD HORNBERGER (*Landw. Versuchs.-Stat.*, 1899, 51, 473—478).—The ash of different parts of the trunk-wood of two copper-beeches, 102 and 105 years old, was found to contain from 0.97 to 1.20, and 0.57 to 0.90 per cent. of baryta (compare *Mündener forstl. Hefte.*, 1898, No. 14, 94). The soil was found to contain a small amount of baryta; 400 grams extracted with hot 5 per cent. hydrochloric acid yielded 9 milligrams of barium sulphate.

Barium was detected by Forchhammer (*Ann. Phys. Chem.*, 1855, [i], 95, 60) in the ashes of beech, oak, and birch, &c., and by Boedeker and Eckhard (*Annalen*, 1856, 100, 294) in beech wood and in the sandstone near Göttingen (compare also Scheele, *Opus. Chem. et Phys. Lips.*, 1788, 1, 258). It also occurs in the Nile mud (Knop, *Landw. Versuchs.-Stat.*, 17, 65) and in wheat grown in the Nile valley (Dworzak, *ibid.*, 398).

N. H. J. M.

**Reducing and Invertible Sugar in the Stalks of Maize.** By CONSTANTIN I. ISTRATI and G. CETTINGER (*Compt. rend.*, 1899, 128, 1040—1043).—In maize, the weight of the stalk diminishes in the inverse ratio of its increase in volume because the assimilation of solid matter is slower than the loss of water. Before inversion and up to 70 days of growth, the juice is generally lævogyrate, but the lævo-

gyrate power gradually diminishes and changes to dextrogyrate, which increases as vegetation advances. The quantity of invertible sugar present is at least twice as great as that of the reducing sugar, and it increases with the age of the plant. The maximum in the green stalks after 94 days growth is about 1·89 per cent., but the proportion in the dry stalk is about 8·62 per cent. C. H. B.

**Reducing and Invertible Sugar of Maize Stalks after Removal of the Ear at the Commencement of Formation.** By CONSTANTIN I. ISTRATI and G. ETTINGER (*Compt. rend.*, 1899, 128, 1115—1117).—Tables are given showing the effect of removing the ears of maize on the amount of sugar contained in the stalks. The weight of the stalks, the sp. gr. of the sap, and the dry weight increase when the ears are removed. In 10 cases out of the 15 species of maize studied, the removal of the ear promotes an increase of invertible sugar; in the five remaining cases, which are those of plants containing the largest quantity of sugar in the normal condition, the removal of the ear brings about an actual decrease in the amount of sugar present. G. T. M.

**Glycollic Acid in the Sugar-cane.** By EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1899, 21, 45—50).—On adding a few drops of nitric acid to sugar-cane juice clarified by means of a slight excess of basic lead acetate, a white, crystalline precipitate is formed; the author shows that this is a mixture of lead salts of glycollic acid. This acid exists as such in the cane, and can be readily isolated by treating the fresh cane-juice with an excess of freshly precipitated cupric hydroxide; the precipitate formed is thoroughly washed with cold water, decomposed with hydrogen sulphide, and the liquid freed from copper sulphide by filtration. The resulting acid filtrate is evaporated until crystals begin to form, when on cooling a solid mass of glycollic acid crystals separates. The quantity of the acid thus obtained corresponds with 75—80 per cent. of the total acidity of the juice. The occurrence of glycollic acid in cane-juice is held to account for (1) the occasional presence of formic acid in the vapours from multiple-effect evaporators, since glycollic acid decomposes below 100°, yielding formic acid. (2) Part, at least, of the colour of low-grade sugar products, as glycollic acid readily chars. (3) The frothing of boiled molasses on standing, the gas to which this is due being evolved in the decomposition of glycollic acid. T. H. P.

**Peptone in Sugar Beet Juices.** By A. RÜMLER (*Bied Centr.*, 1899, 28, 358; from *Deut. Zuckerind.*, 1898, 302, and *Oesterr. Zeits. Zuckerind.*, 1898, 270).—Peptones were detected in various intermediate products of the manufacture of sugar. It is supposed that peptones behave like amido-acids, showing both acid and alkaline reaction, and combining both with acids and bases. It is possible that, when juices containing lime are treated with sulphurous acid, peptones and also proteids, which resemble peptones in several respects, are precipitated along with calcium sulphite. N. H. J. M.

**Girard's Researches on Caoutchouc Milk.** By LÉON LINDET (*Bull. Soc. Chim.*, 1898, [iii], 19, 812—815).—This is an account of the

results, hitherto unpublished, obtained by the late AIME GIRARD. From whatever source obtained, caoutchouc milk presents the appearance of a white, somewhat viscous, milky liquid, which is seen by the microscope to consist of a multitude of globules, having a diameter of  $3-5\mu$ , suspended in a clear serum. The sp. gr. of the latter, freed from caoutchouc, varies between 1.037 and 1.040. On adding to the "milk," with constant agitation, an equal volume of 95 per cent. alcohol, the globules run together, and the mass of caoutchouc thus formed can be separated and weighed. The following results were thus obtained from a number of specimens :

Source.	Sp. gr.	Caoutchouc per cent.
Pernambuco ( <i>Haucornia speciosa</i> ) ...	0.990	31.6
African lianas .....	0.987	33.4
Para ( <i>Siphonia elastica</i> ) .....	0.986	42.6
Nicaragua ( <i>Castilloa elastica</i> ) .....	0.980	32.3
Algeria ( <i>Ficus macrophylla</i> ) .....	1.000	37.5
" ( " " ) .....	1.005	37.1
" ( " <i>elastica</i> ) .....	1.001	17.3
" ( " <i>nitida</i> ) .....	0.971	31.3
" ( " <i>lævigata</i> ) .....	1.005	28.0
New Caledonia ( <i>Kickxia Africana</i> )...	1.005	27.0

The coagulation of the "milk" is in practice brought about by heating, with or without the addition of alum, common salt, sulphuric acid, lemon juice, vegetable infusions, &c. Good results are also obtained by heating the "milk" at  $50^{\circ}$  and agitating in a churn.

N. L.

**Wines obtained by Heating before Fermentation.** By AUGUSTÉ ROSENSTIEHL (*Compt. rend.*, 1899, 128, 1050—1052).—The author has compared on a large scale the properties of wines prepared from must that has previously been heated (*Abstr.*, 1897, ii, 339) with wine prepared in the ordinary way. The preliminary heating increases the yield of juice from a given quantity of grapes, and both the unfermented juice and the wine prepared from it are deeper and richer in colour than wine obtained from the same grapes in the usual way ; the wines from the heated must also have more body, and are superior in flavour.

The sterilised musts were fermented with yeasts of various definite kinds, and always gave a higher alcoholic strength than the unheated musts. No differences in flavour were observed with different yeasts, and it would seem that there is no advantage in using yeast exclusively of one species. Cultivated yeasts, however, always gave somewhat better results than crude yeast. The wines from the heated musts were always found to be free from the disease known as "turning," whilst other wines made in the same place were infested with the germs of this disease.

C. H. B.

**Effect of the Amount of Water and the Richness of Soil on the Development of the Roots and Above-ground Growth of Oats.** By M. TUCKER and CONRAD VON SEELHORST (*Bied. Centr.*, 1899, 28, 269—273 ; from *J. Landw.*, 1898, 46, 52).—The experiments

were made in zinc vessels containing 17,130 grams of soil (dry). There were three series ; with (1) 12·35, (2) 15·41, and (3) 16·44 per cent. of water, and each series included pots without manure and with different amounts of various manures.

Production of grain and straw increased with the amount of water supplied, whilst the amount of roots diminished. With the least amount of water, the development of the roots was greatest, both absolutely and relatively, but the increased amount of roots was unable to supply the amount of food, and especially water, necessary for the production of a corresponding amount of straw and grain. With more water, a smaller quantity of root was able to furnish a greater amount of nutritive matter and water to the above ground growth.

Deficiency of phosphoric acid induced relatively increased production of roots, but, as in the case of deficiency of water, the increased amount of root was unable to compensate for the poorness of the soil. Abundance of manure increases the amount of both roots and above-ground growth ; the increase in straw and grain is, however, greater than that of roots, so that in presence of manure a given amount of roots produces more straw and grain than in its absence.

With increased supply of water, and with manure, the proportion of above-ground growth to roots is considerably increased. Without manure and with 14·35 per cent. of water in the soil, the relation of the amount of root to that of grain and straw was 1:5·41. With the same amount of water and with manure ( $P_2O_5$ ,  $K_2O$ , and N) the relation was 1:6·43. With 16·44 per cent. of water, the relations were 1:9·41 and 1:16·16 without and with the same manure respectively.

N. H. J. M.

**Digestibility of Various New Foods and the Changes produced in them when superheated.** By BERNHARD SCHULZE (*Bied. Centr.*, 1899, 28, 287—288 ; from *Jahresber. agric. chem. Versuchs-Stat.*, Breslau, 1896).—The following percentage amounts of proteids were digested in gastric and pancreatic juice :

1. Residues of the manufacture of wheat starch	98
2. Fish freed from fat .....	94—97·1
3. Mixture of potato pulp (80) and molasses (20 per cent.).....	76·2

The digestibility of the residues from the manufacture of alcohol from maize may be considerably diminished by superheating, but residues which are merely darkly coloured do not differ much in digestibility from light-coloured residues. The digestibility coefficients as determined were : light-coloured residues, 70·4 ; moderately-coloured, 69·7 ; dark brown, 67·7 ; superheated and partially burnt, 62·5 and 45·2 per cent.

N. H. J. M.

**Molasses as Cattle Food.** By DICKSON and L. MALPEAUX (*Bied. Centr.*, 1899, 28, 327—328 ; from *Ann. Agron.*, 1898, 24, 353).—Experiments in which sheep, pigs, and bullocks were fed without and with molasses in addition to other foods showed in each case an increase in live weight under the influence of the molasses. With

cows, no change was observed as regards amount and composition of the milk, but the weight of the cows increased somewhat more than without molasses. The food was also found to be suitable for horses when given with lucerne hay and wheat straw as a substitute for a portion of the oats. Attention is directed especially to the use of molasses as an addition to inferior hay, which would otherwise not be consumed. The molasses contained: sugar, 46; nitrogenous matter, 11.56; water, 26.8; and ash, 9.45 per cent.

N. H. J. M.

**Investigations of Soils.** By BERNHARD SCHULZE (*Bied. Centr.*, 1899, 28, 286; from *Jahresber. agric. chem. Versuchs-Stat. Breslau*, 1896).—Analyses are given of (1) two Bulgarian soils, and (2) of two soils from Asia Minor. The former are very deep soils, whilst the latter are marl soils which produce two crops yearly, notwithstanding imperfect methods of cultivation. The results given are percentages in dry substance.

		Organic Matter.	N.	K <sub>2</sub> O.	CaO.	P <sub>2</sub> O <sub>5</sub> .
1. Bulgaria .....	a.	6.28	0.157	0.289	1.37	0.291
	b.	17.23	0.801	1.141	2.62	0.475
2. Asia Minor...	a.	—	0.305	0.590	20.53	0.093
	b.	10.43	0.267	0.457	11.41	0.176

N. H. J. M.

**Injurious Effect of Sea-water on Soil.** By A. J. SWAVING (*Landw. Versuchs-Stat.*, 1899, 51, 463—471).—In consequence of the high tide and the strong wind on December 23—24, 1894, the sea dams of Zealand and South Holland partly collapsed and let in the sea. Samples of soil, and of the water of the ditches, were taken at different times for determining the chlorine in order to ascertain to what extent the resulting infertility of the soil was due to the presence of sodium chloride. It was found that, whilst in one case the soil, to a depth of 25 cm., contained as much as 6.220 per thousand of chlorine, in two other cases only 0.533 and 1.340 per thousand were present, and that in the course of a year the amounts were greatly diminished.

The unsatisfactory condition of the crops on the flooded land was due partly to the washing out of the soil, and partly to the mechanical action of the sea and the deposition of mud resulting in the formation of hard crusts which hindered the washing out of the sodium chloride, and sometimes prevented germination of seeds. Storp (*Abstr.*, 1884, 856) showed that solutions of sodium chloride cause soils to lose certain manure-constituents.

N. H. J. M.

**The Causes and the Importance of the Destruction of Nitrates in Soil.** By W. KRÜGER and W. SCHNEIDEWIND (*Ann. Agron.*, 1899, 25, 249—251; from *Landw. Jahrb.*, 1899, 217—253. Compare this vol., ii, 449).—Whilst straw, owing to pentosans present, is especially favourable in promoting denitrification, other compounds, such as sugar, glycerol, citrates, malates, &c., also facilitate the activity of the microbes. Peat, however, is inert. Other conditions favourable to denitrification are excess of moisture—the loss is considerable in submerged soil—and high temperature. In practice, the loss of nitrogen is probably much less than in small experiments.

In the field, the conditions are more favourable to nitrification than is the case with pot experiments, and the amount of nitrates applied in farmyard manure is far greater than the loss.

P. P. DEHERAIN (*ibid.*, 251) considers that the question of denitrification is not sufficiently important to justify the amount of labour expended on it in Germany, and refers to Breal's results (*Abstr.*, 1892, 1259; 1896, ii, 444; and *Ann. Agron.*, 23, 49, and 24, 130), and to his own indicating that addition of starch to soil causes loss of nitrates (*Abstr.*, 1898, ii, 630).

N. H. J. M.

**Specific Manurial Requirements of Crops.** By FERDINAND WOHLTMANN (*Bied. Centr.*, 1899, 23, 314—315; from *Fühling's Landw. Zeit.*, 1898, 47, 13).—The following conclusions are drawn from the results of experiments on small plots. The soil was a heavy loam.

Dung produced large and healthy crops with cereals, and especially with rape, and improved the soil physically. Lime acted differently with different crops; it gave better results with wheat than with rye and was injurious to maize, clover, and potatoes. Phosphoric acid, as double superphosphate, injured beans, which ripened too soon and had yellow leaves. Kainite produced, with all crops, lighter coloured leaves, and in the case of sugar beet increased the percentage of sugar; it has, however, a very injurious effect on the soil which has to be remedied by applying lime. Ammonium sulphate generally gives greater yields than sodium nitrate, especially with winter cereals. In rainy seasons, as much as 20 per cent. of sodium nitrate may be lost, and there is never any after-effect such as that observed with ammonium sulphate on clover.

N. H. J. M.

**Use of Artificial Manures for Forcing-House Crops.** By EDWARD H. JENKINS and W. E. BRITTON (*Ann. Rep. Agric. Expt. Stat., Connecticut*, 1896, 20, 205—229).—The soils employed were: (1) turf previously mixed with stable manure, and (2) coal ashes mixed with pure calcium carbonate and moss peat. The manures were well mixed with the soils.

The greatest yield of tomatoes was obtained with the following amounts of manures per 100 square feet (8 inches deep): Sodium nitrate, 4.7; dissolved bone black, 0.94; and potassium chloride, 1.13 lbs. With this manuring, the coal-ash soil gave a greater yield than was produced in a rich compost, with or without further addition of artificial manure.

Radishes also grew well in coal ashes with peat and manures, and developed more quickly than in compost. Similar results were obtained with carnations. With cucumbers, a greater yield was obtained in ashes, with artificial manures, than in compost, and the average weight of the single cucumbers was also greater. Sodium nitrate and cotton seed meal were about equally efficient in coal ashes, but in compost the meal gave better results.

N. H. J. M.

**Manurial Experiments with Flowers.** By JOHN SEBELIEN (*Bied. Centr.*, 1899, 23, 315—321; from *Gartnertitende*, 1898).—Experiments in which pelargonias, fuchsias, and heliotropes were variously manured showed that diluted liquid manure and potassium



phosphate had no effect, whilst sodium nitrate, and mixed manures containing a good deal of nitrogen, had considerable effect on the development of the flowers and vegetative organs. Subsequent experiments with pelargonias manured with the same amounts of nitrogen, but varying amounts of other constituents, showed that a complex manure gave better results than nitrogen alone. The least amount of nitrogen (4.23 grams) gave the best results; twice that quantity was injurious, whilst 16.92 grams was poisonous.

Exclusive nitrogenous manuring produced plants poor in lime, magnesia, phosphoric and sulphuric acids, and nitrogen, whilst the percentage of potash was high. The average percentage composition of the ash of pelargonias manured with the smallest amount of nitrogen in conjunction with other manure constituents was as follows:

K <sub>2</sub> O.	CaO.	MgO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	Cl.
18.21	21.05	2.34	10.80	7.87	6.13

The dry substance contained: N, 3.29, and ash, 13.44 per cent.

N. H. J. M.

**Experiments with Nitragin.** By ANDREW P. AITKEN (*Trans. Highland and Agric. Soc. Scotland*, 1898, [v], 10, 299—305).—Experiments with vetches, made by Shirra Gibb at Boon, in which nitragin was applied to the soil, gave a very slight increase of produce as compared with the yield obtained without inoculation. The differences are attributed to "accident." On taking up plants from the different plots (without and with inoculation), it was found that some had many large, whilst others were almost free from, nodules, the nodules also varying in size; these differences, however, occurred in all the plots, whether inoculated or not. In experiments at Linhead, Cockburnspath, with beans and vetches grown together, less grain and more straw were obtained when nitragin was applied than without. Several other experiments were made with clover, but the results were all negative.

N. H. J. M.

**Ammonium Sulphate and Sodium Nitrate [as Manures].** By E. KLOEPFER (*Bied. Centr.*, 1899, 28, 309—314; from *Unters. üb. d. Wirk. d. schwefels. Ammoniak u. d. Chilisalpeters, Essen*, 1898).—Whilst sodium nitrate is liable to loss in drainage, ammonia is absorbed and nitrified, and is available to vegetation for a long time. On the other hand, application of ammonium salts often necessitates application of lime, and warm weather is required for nitrification. Nitrate is objectionable on heavy soil by causing the surface to become caked. Ammonium sulphate is preferable for autumn manuring and for oats.

N. H. J. M.

**Conservation of the Nitrogen of Farmyard Manure.** By CASIMIR V. ROGOVSKY (*Ann. Agron.*, 1899, 25, 244—248; from *Inaug. Diss. Leipzig*).—Artificial farmyard manure was prepared by mixing cow-dung (61.7), liquid manure (26.7), and straw (11.6 parts), and was kept in quantities of 6 kilograms for 56 days, both alone and with different amounts of various substances, such as a mixture of sulphuric and hydrofluosilicic acids (a bye-product of the manufacture

of aluminium), chalk, chalk and soil, and soil alone. The loss of nitrogen in the manure alone was 36.6 per cent. The addition of acids much diminished the loss, and to a greater extent than could be accounted for by merely combining with the ammonia; this biological action is attributed to the hydrofluosilicic acid. Chalk was very effective in preserving nitrogen, but its action was irregular, whilst soil alone had only a slight effect.

The examination of the nitrogenous matter by Stutzer's copper hydroxide method gave results indicating that the non-assimilable nitrogen increased by 25.6 in the manure treated with acid and by 41.2 when treated with soil. Subsequent experiments, however, in which mustard was manured with the different manures showed that the nitrogen had not become non-assimilable, and that the amount of produce was much higher where the loss of nitrogen had been least. It is concluded therefore that, not only proteids, but also certain amides, are precipitated by Stutzer's method.

The conclusion also is drawn that only the nitrogen of the liquid manure is available to plants, that of straw and fæces being without effect.

Less water is necessary to produce 1 gram of dry substance when highly nitrogenous manure is present than with less nitrogen.

P. P. DEHERAIN (*ibid.*, 248) considers that the method employed is unsuitable, as with only 6 kilograms of manure the temperature would not rise sufficiently to produce enough carbonic anhydride to retain the ammonia; and the conditions as regards access of air are quite different in such small amounts as compared with heaps containing several cubic yards. Whilst it is of interest that in the time over which the experiments extended only the nitrogen of the liquid manure was utilised, there can be no doubt that the nitrogenous matter of the fæces, originally insoluble, gradually becomes available as time goes on.

N. H. J. M.

**Effect of Nitrate on the Development of Barley.** By DM. N. PRIANISCHNIKOFF and S. M. KOUZNEZOFF (*Ann. Agron.*, 1899, 25, 254—256; from *Izv. Moscow Selskokhov. Inst.*, 3, 1897, ii, 53).—Experiments similar to Hellriegel's were made with oats grown in sand and manured with various amounts of sodium nitrate in addition to ash constituents. The results show a regular increase of produce with increased addition of nitrate up to a certain point, after which an excess of nitrate is injurious. The nitrate was most completely utilised when given in the smallest amounts. With very small quantities of nitrate, the results indicate that there was possibly a very slight fixation of free nitrogen, presumably under the influence of algæ.

N. H. J. M.

**Perchlorate in Chili Saltpetre.** By B. SJOLLEMA (*Bied. Centr.*, 1899, 28, 286—287; from *Deut. Landw. Presse*, 1897, No. 22, 195. Compare Abstr., 1897, ii, 585).—In reply to Wagner (Abstr., 1898, ii, 252), the author states that he only suggested (having no experimental evidence) that 0.5 per cent. of perchlorate is probably injurious. Experiments in which 150—200 kilos. of nitrate containing 1.4 per cent. of perchlorate was applied per hectare showed that rye was much injured by this amount. It is, however, difficult to estimate

exactly the amount of perchlorate in sodium nitrate, owing to its uneven distribution.

Other plants seem to be injured less than rye by perchlorate. It is possible that quantities of perchlorate too small to produce visible injury may diminish the yield of a crop.

De Caluwe's experiments with six kinds of Chili saltpetre indicated that, whilst 6 per cent. of perchlorate was very injurious to rye, even 1 per cent. injured the plants. The effect of the perchlorate was only seen 4—5 months after the application of the manure; the plants had been exposed to very heavy rain in the winter months.

N. H. J. M.

**Relative Value of Mineral Phosphates.** By DM. N. PRIANISCHNIKOFF (*Ann. Agron.*, 1899, 25, 177—187).—Sand culture experiments, in which cereals were manured with various phosphorites, showed that the phosphoric acid was only available to a slight extent. Under the same conditions, certain other plants, such as peas, lupins, buckwheat, and mustard, were able to utilise the phosphoric acid of the phosphorites (compare Schreiber, *Bied. Centr.*, 1897, 26, 803). Certain soils have the property of rendering phosphorites available for cereals and other plants; of the soils examined, the so-called "podzols" (which consist of very fine siliceous matter mixed with some organic matter) were the most effective, and forest and peaty soils also had the same property. The black soils of Kherson and Nidjni-Novgorod, &c., are without action on phosphorites, and it is supposed that soils originally "active" would become inactive after some years of cultivation sustained by farmyard manure. Further experiments will, however, be necessary.

In analysing phosphorites to ascertain their manurial value, it will be necessary to take into account the conditions under which they are to be employed. A method suitable for indicating the value when applied to cereals on "inactive" soil would obviously be unsuitable in the case of cereals on active soil, or of other plants on any soil, and *vice versa*.

N. H. J. M.

**Composition of the Insoluble Portion of Basic Slag.** By MAX PASSON (*Bied. Centr.*, 1899, 28, 350—351; from *Landw. Centr. Posen*, 1898, No. 23, 193).—About 500 residues of basic slag, after extraction by Wagner's citrate method, were carefully mixed and analysed. The following percentage results were obtained:—water, 1·00; phosphoric acid, 9·22; phosphoric acid soluble in citric acid, 4·40; lime, 33·75; fine meal, 72·76. The coarse meal contained 12·46 per cent. of total, and 7·48 per cent. of citrate-soluble, phosphoric acid; the fine meal 7·93 and 3·46 per cent. respectively. This result is supposed to be due to the fine meal being more readily extracted in the Wagner process.

N. H. J. M.

**Composition of the Waters of Danish Rivers.** By T. WESTERMANN (*Bied. Centr.*, 1899, 28, 291—293; from *Tidsskr. Landbr. Planteavl*, 1898, 4, 157—165).—Samples of water from the different rivers were analysed in November, 1889 (the time of the year when

the land is irrigated), and again in May and August, 1892. The following results show the average composition in parts per million :

	Nitrogen.					CaO and		
	N <sub>2</sub> O <sub>5</sub> .	NH <sub>3</sub> .	Organic.	Total.	K <sub>2</sub> O.	MgO.		P <sub>2</sub> O <sub>5</sub> .
Susaa.....	0·96	1·21	1·78	3·95	2·65	111·8		(0·2)
Odenseaa ...	0·62	1·22	1·21	3·05	2·98	120·4		(0·26)
Storaa .....	traces	1·22	0·67	1·96	1·46	37·1		(0·3)
Skernaa.....	(0·2)	1·46	0·92	2·45	1·69	25·4		(0·2)
Kongesaa.....	(0·35)	0·95	1·01	2·07	1·41	52·0		(0·2)
Gudenaa .....	(0·17)	1·48	0·64	2·25	1·95	51·8		(0·2)

The numbers in brackets were obtained in 1889; the subsequent samples only contained traces of the constituent.

The nitrates in the November samples are doubtless derived from the manure applied to the fields. It is estimated that the Susaa, with a flow of 200 cubic feet per second, carries away N, 15,400 cwt.;  $K_2O$ , 10,300 cwt., and CaO and MgO, 436,000 cwt. yearly.

N. H. J. M.

**Lysimeter Experiments.** By JOSEPH HANAMANN (*Bied. Centr.*, 1899, 28, 303—305; from *Zeits. landw. Versuchsw. Oesterr.*, 1898, 1, 399).—The experiments were conducted in metal vessels with a surface of 1 square metre and 50 cm. deep. There were 6 vessels with the same soil, 1 without, and 5 with vegetation. The following amounts (in grams) of constituents were washed out by drainage from April to October, 1896, when the rainfall was unusually high.

	Bare soil.	Red clover.	Barley.	Sugar-beet.	Maize.	Beans.
$N_2O_5$ .....	1·7309	0·0749	0·0661	0·0097	0·0097	0·0091
$K_2O$ .....	0·1457	0·0688	0·1161	0·1256	0·0734	0·1105
$Na_2O$ .....	0·1540	0·1025	0·1161	0·1780	0·1094	0·1243

Experiments were also made with three other soils without vegetation.

The loss of chlorine was much less in cultivated than in bare soil, but the loss of sulphuric acid was only slightly greater without than with vegetation. Phosphoric acid is retained by soil more tenaciously than any other nutritive constituent.

N. H. J. M.

### Analytical Chemistry.

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Novelties in Laboratory Utensils. By A. GAWALOWSKI (*Zeit. anal. Chem.*, 1899, 38, 237—242).—These include a burette jet requiring no pinch clamp, and possessing advantages over those of Leybold and Mohr; an improved form of Erdmann's float containing a roll of aluminium foil with horizontal lines cut through it instead of the usual diamond scratch; a simple burette holder, constructed of two pieces of thin brass plate; a pinch-clamp which can be removed without disconnecting the tubes; and a still for the preparation of

sterilised distilled water, on the principle of passing the steam through a coil at a high temperature before condensing it. M. J. S.

**A New Filtering Medium.** By GEORGE WILLIAM SARGENT and JOHN KIRK FAUST (*J. Amer. Chem. Soc.*, 1899, 21, 287—288).—For the separation of manganese dioxide from a nitric acid solution in the analysis of steels, the authors recommend a carbon-filtering tube, plugged with glass-wool covered with a layer of "pewter sand" and a thin layer of asbestos. A similar sand filter may also be used with advantage in separating ammonium phosphomolybdate. T. M. L.

**Estimation of Hydrochloric Acid in the Contents of the Stomach.** By HANS LEO (*Chem. Centr.*, 1899, 1, 61—62; from *Zeit. Klin. Med.*, 36, 76—84).—A controversy with Sjöqvist as to the influence of potassium dihydrogen phosphate when estimating free hydrochloric acid by means of barium carbonate (compare *Abstr.*, 1896, ii, 496). L. DE K.

**Detection of Small Quantities of Bromine in Chlorides.** By HENRI BAUBIGNY (*Compt. rend.*, 1899, 128, 1160—1163).—When relatively large quantities of sodium or other chloride containing small quantities of bromide are treated at the ordinary temperature in the manner previously described (*Abstr.*, 1898, ii, 90 and 137), small quantities of chlorine are liberated with the bromine. The liquid in which the vapours have been absorbed must therefore be treated at 100° in the ordinary manner (*loc. cit.*), when the bromine only is liberated. C. H. B.

**Separation and Estimation of Bromine in the Presence of Excess of Chlorides.** By HENRI BAUBIGNY (*Compt. rend.*, 1899, 128, 1236—1238).—A solution of the salt to be analysed, mixed with potassium permanganate and sufficient hydrochloric acid to decompose all the bromide present, is distilled in a current of air, and the volatile products received in a solution of caustic alkali. Under these conditions, one drop of hydrochloric acid suffices to liberate all the bromine from several milligrams of bromide. The remainder of the analysis is carried out in accordance with the method already indicated (preceding abstract). G. T. M.

**Detection and Colorimetric Estimation of Traces of Iodine in Organic Matters.** By PAUL BOURCET (*Compt. rend.*, 1899, 128, 1120—1122).—The substance is thoroughly disintegrated, moistened with caustic potash solution, and dried at 100°; the dried mass is then pulverised and fused with caustic potash in a nickel crucible. The product of fusion is extracted with hot water, and the aqueous extract cooled and treated with 20 per cent. sulphuric acid; when the neutral point is reached, the solution is again rendered alkaline with potash, and then added to an equal volume of 95 per cent. alcohol. The greater part of the potassium sulphate is precipitated, and on concentrating the mother liquor and repeating the treatment with alcohol, the sulphate is finally removed. The mother liquor is concentrated to 2 or 3 c.c. and treated with nitric oxide gas in the presence of carbon bisulphide. The colorimetric estimation is made

according to the method suggested by Rabourdin and Nielloux. A table is appended giving the amount of iodine in milligrams per kilo. in a series of edible fish. G. T. M.

**Apparatus for obtaining Synchronous Gaseous Currents in the Estimation of Atmospheric Gases.** By FELIX MARBOU-TIN and ADRIEN PECOUL (*Bull. Soc. Chim.*, 1898, [iii], 19, 819—820).—A U-tube containing mercury and provided with a bulb in each limb. is made to oscillate round an axis perpendicular to its plane by means of a suitable motor. The bulbs, which are of equal size, alternately fill and empty themselves, and thus regulate the flow of gas to the aspirators with which they are connected. If a clockwork movement is employed, the two currents are not only synchronous but also isochronous. N. L.

**Estimation of Sulphur in Pyrites in the Presence of Iron.** By OLE N. HEIDENREICH (*Zeit. anorg. Chem.*, 1899, 20, 233—234).—The solution of the pyrites prepared in the ordinary way by heating with nitro-hydrochloric acid and evaporating three times with hydrochloric acid, is diluted with hot water to about 250 c.c. and then treated with metallic zinc until all the iron is reduced to the ferrous state. The precipitation of the sulphur is effected in the filtered solution in the ordinary way by means of barium chloride. The results are accurate, since the ferrous salt does not come down with the barium sulphate. This method is much simpler than that proposed by Küster and Thiel (this vol., ii, 247). E. C. R.

**Estimation of the Total Sulphur in Coal.** By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1899, 29, 181—184).—One part of the finely powdered coal is intimately mixed with 4 parts of manganese dioxide, 1 part of potassium permanganate, and 2 parts of sodium carbonate; the whole is then placed in a platinum crucible, covered with a thin layer of the oxidising mixture, and heated gradually until the bottom of the crucible is just reddened. After half an hour's heating, the mass is allowed to cool, and is then poured into 40—50 c.c. of water, which is afterwards acidified with nitric acid and boiled. The liquid is filtered, and the sulphuric acid in the filtrate estimated by precipitation with barium chloride. A blank experiment with the oxidising mixture alone is advisable, as manganese dioxide often contains small quantities of sulphur.

Comparative experiments show that the method yields results identical with those given by Eschka's process, which is the one generally employed, and has the advantage over the latter of occupying much less time. T. H. P.

**Estimation of Sulphur in Sulphites.** By A. BOURGOUGNON (*J. Amer. Chem. Soc.*, 1899, 21, 469—470).—The weighed sulphite is dissolved in water, and to the solution is added a sufficient quantity of a mixture of water, hydrochloric acid, hydrogen peroxide, and barium chloride. After gentle heating, the sulphuric acid is estimated in the usual way. As commercial hydrogen peroxide frequently contains sulphuric acid, the reagent to be used may be prepared as follows. Hydrated barium peroxide is added in small quantities at a time to very dilute hydrochloric acid until the liquid is alkaline, alumina and

ferric oxide being thus precipitated; the liquid is filtered, and the filtrate, collected in hydrochloric acid, is ready for use. T. H. P.

**Estimation of Sulphuric Acid, with Especial Reference to the Estimation of Sulphur in Iron Ores and the Products of the Metallurgy of Iron.** By C. MEINEKE (*Zeit. anal. Chem.*, 1899, 38, 209—217).—To obviate the well-known error in the estimation of sulphuric acid in solutions containing much ferric chloride, the latter is reduced by zinc. To apply the method to pyrites residues, 2.5 grams of the substance is dissolved in hydrochloric acid and potassium chlorate; the chlorine is expelled; zinc in the form of granules or coarse filings is added, and when reduction is complete the solution is filtered and is then ready for precipitation with barium chloride. A pure white precipitate is obtained, the weight of which agrees closely with that obtained by Schröder's more tedious, but admittedly accurate, method of fusion with sodium carbonate and potassium chlorate. The same process serves for the estimation of sulphur in pig-iron, and the results are identical with those yielded by the author's cupric chloride method (*Abstr.*, 1871, 89). M. J. S.

**Volumetric Estimation of Combined Sulphuric Acid.** By FELIX MARBOUTIN and MARCEL MOLINIE (*Bull. Soc. Chim.*, 1898, 19, [iii], 713—714 and 714—717).—Marboutin's volumetric method for estimating combined sulphuric acid (*Abstr.*, 1898, ii, 254) is preferable to Telle and Robin's (*Abstr.*, 1898, ii, 451 and 452), the appreciable solubility of barium chromate not having been taken into account in the latter; the error thus introduced may amount to 10 per cent. on the  $\text{SO}_3$  present.

Marboutin's method of estimating combined sulphuric acid may be applied to a water containing organic matter, provided that it is evaporated with dilute nitric acid, and the residue treated with the fuming acid. The excess of nitric acid is removed by evaporating to dryness in the presence of hydrochloric acid, and the final residue is extracted with water and treated in the manner previously described (*Abstr.*, 1898, ii, 254). As an alternative method, the organic matter is destroyed by Villiers' method (*Abstr.*, 1898, ii, 492); the sulphuric acid is then estimated gravimetrically, because the presence of the manganese or vanadium salts employed would interfere with the volumetric process. In order to ensure rapid filtration, the liquid and the precipitated barium sulphate are digested for 12 hours at  $40^\circ$ .

G. T. M.

**Influence of Hydrochloric Acid on Titrations with Sodium Thiosulphate, with Especial Reference to the Estimation of Selenious Acid.** By JOHN T. NORTON, jun. (*Amer. J. Sci.*, 1899, [iv], 7, 287—293; *Zeit. anorg. Chem.*, 1899, 20, 221—229).—Relatively large quantities of sodium thiosulphate can be accurately titrated with iodine in the presence of hydrochloric acid only under special conditions. The temperature of the solution must be maintained as near  $0^\circ$ , and the titration must be performed as quickly as possible. If the quantity of thiosulphate does not exceed 20 c.c. of  $N/10$  solution, it can be easily titrated in the presence of an amount of hydrochloric acid



not exceeding 10 c.c. If, however, a large quantity of thiosulphate is present, a smaller quantity of hydrochloric acid must be used, and the solutions must be considerably diluted. An increase in the quantity of hydrochloric acid, the time taken for titration, and an increase in the temperature of the solution, all tend to give results above the correct one.

The estimation of selenious acid by means of thiosulphate and iodine is accurate when the above conditions are maintained. The quantity of thiosulphate solution must not exceed 20 c.c. of an *N*/10 solution, the hydrochloric acid must not exceed 10 c.c. (sp. gr. 1.12), and the solution before beginning the titration must be diluted to 400 c.c. If only 5 c.c. of hydrochloric acid are used, the solution need not be diluted to more than 200 c.c.

Muthmann and Schäfer (Abstr., 1893, ii, 318) estimate selenious acid by adding to the solution an excess of potassium iodide containing hydrochloric acid and titrating the liberated iodine with thiosulphate solution. The author finds that accurate results are more easily obtained by employing a larger excess of potassium iodide and then estimating the precipitated selenium gravimetrically. E. C. R.

Possible Error in the Estimation of Nitrogen in Nitrates due to Impurities in Reduced Iron. By B. L. HARTWELL and HOMER J. WHEELER (*J. Amer. Chem. Soc.*, 1899, 21, 468—469).—The Ulsch method of estimating nitrogen in nitrates involves the use of reduced iron, a so-called chemically pure specimen of which the authors find to contain some nitrogenous substance. The error caused is very appreciable. A similar case has been investigated by Brandt (*Chem. Zeit.*, 1899, 23, 22), who found that the impurity is removed by heating the iron in a current of hydrogen, but not by extraction with water, alcohol, or ether. T. H. P.

Modification of Pierce's Method for the Estimation of Arsenic in Ores. By J. F. BENNETT, jun. (*J. Amer. Chem. Soc.*, 1899, 21, 431—435).—About half a gram of the finely powdered ore is mixed with from six to ten times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate and the mass gradually heated to fusion, which is maintained for some minutes. On cooling, it is extracted with boiling water and filtered; the filtrate, containing the arsenic as alkali arsenate, is strongly acidified with acetic acid, and boiled to expel carbonic anhydride. After cooling, phenolphthalein is added, then sodium hydroxide solution until alkaline, and finally acetic acid until just acid; a slight excess of silver nitrate solution is now added, the liquid being kept stirred and the precipitate allowed to settle, exposure to direct sunlight being avoided. After a few minutes, the clear liquid is poured on to the filter, the precipitate being washed with cold water first by decantation and finally on the filter. The precipitate is then dissolved in fairly concentrated nitric acid, the solution made up to 100 c.c. and titrated with standard thiocyanate; the silver may also be determined by igniting the filter and precipitate and cupelling. T. H. P.

Estimation of Arsenic in Glycerol. By A. C. LANGMUIR (*J. Amer. Chem. Soc.*, 1899, 21, 133—136).—The organic matter is

oxidised by evaporation with a mixture of 200 c.c. of nitric acid and 12 c.c. of sulphuric acid; the residue is transferred to a Marsh's apparatus, and the arsenic separated by heating the escaping gas, when a mirror is formed in a constricted part of the exit tube. The tube is cut and weighed to 0.01 milligram on an assay balance, then dipped in hot dilute nitric acid to remove the arsenic, and again weighed. In a trial experiment, 0.50 milligram of arsenic was taken and 0.45 milligram separated and weighed.

A rough estimate of the amount of arsenic may be obtained by adding zinc and hydrochloric acid to the diluted glycerol in a test-tube which is closed by a loosely-fitting cork covered with a filter paper; the filter paper is moistened with mercuric chloride, and shows a yellow stain if arsenic is present. The stain is permanent, and a series of specimens may be kept showing the coloration with different weights of arsenic. The colour is quite distinct with 0.01 milligram of arsenic, and is perceptible with 0.0025.

T. M. L.

**Tests for Boric Acid.** By VICTOR LENHER and JAMES S. C. WELLS (*J. Amer. Chem. Soc.*, 1899, 21, 417—420).—Of the various qualitative tests for boric acid, the pink coloration given to turmeric paper is the most delicate. An improvement on the ordinary method of carrying out the green flame test is to heat the mixture of borate, sulphuric acid, and alcohol in a test-tube fitted, by means of a cork, with a glass jet; the issuing gas is caused to impinge on the flame of a Bunsen burner, which then shows the characteristic green tint.

T. H. P.

**Silica and Insoluble Residue in Portland Cement.** By PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1899, 21, 289—291).—In the estimation of silica in low-grade cements by solution in hydrochloric acid and evaporation to dryness, abnormally high results are often obtained, when compared with those obtained by the fusion method of estimating silica. This is due to the presence in the cement of unconverted silica and alumina, owing to the imperfect burning of the clay, and is a possible source of error in the analysis, but the difference between the silica determinations by the two methods may also be used as a test of the quality of the cement, since in a good sample the difference never exceeds 0.20 per cent., whilst in poor samples it may amount to as much as 4.5 per cent.

T. M. L.

**Use of Compressed Oxygen and Soda-lime in Organic Analysis.** By FRANCIS G. BENEDICT and OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1899, 21, 389—398).—The authors recommend compressed oxygen drawn directly from the steel cylinder for use in combustions. The device for regulating the flow of the gas consists of a T-piece so arranged that one end of the cross-tube dips about 1 inch under mercury, the other end being connected to the purifying apparatus; the rate of flow is then adjusted by a pinch-cock on a piece of rubber tubing, any slight excess of oxygen escaping through the mercury trap. For removing carbonic anhydride from the oxygen and for collecting that produced in the combustion, soda-lime prepared as follows gives good results: 1 kilogram of commercial

caustic soda is treated in an iron vessel with about half a litre of water; to the thin paste formed, while still hot, is added 1 kilogram of coarsely-powdered quicklime, the mixture being well-stirred; the mass soon heats and must be stirred and the lumps broken up. When cool, it is ready for use. U-Tubes packed with such soda-lime not only absorb carbonic anhydride as effectively as potash bulbs, but are cheaper and more easily manipulated. T. H. P.

**Estimation of Combined Carbonic Acid or Calcium Carbonate in Soils.** By ALBERT STUTZER and R. HARTLEB (*Zeit. angew. Chem.*, 1899, 448—451).—The authors estimate the amount of calcium carbonate in soils by distilling with a solution of ammonium chloride, taking care that there is at least 10 parts of the latter to one part of calcium carbonate. Ammonium carbonate is liberated, and is, as usual, collected in standard acid and titrated. A check analysis should be made by distilling without addition of ammonium chloride.

Any magnesium carbonate counts as calcium carbonate. Ferrous carbonate, which interferes with the process, may be decomposed by boiling the soil with water for half an hour. The process has been tested side by side with the old method of liberating the carbonic acid and absorbing it in aqueous potash, with satisfactory results. L. DE K.

**Flame Reaction of Potassium in Silicates.** By GRENVILLE A. J. COLE (*Geol. Mag.*, 1898, 5, 103—106).—In Szabó's approximate quantitative estimation of alkalis in silicates by the flame test, the assay is mixed with gypsum. In place of gypsum, sodium carbonate is here suggested, and the flame is viewed through a plate of blue glass 5 mm. thick. Three grades, corresponding with about 4, 8, and 12 per cent. of potash respectively, are distinguished by the intensity of coloration of the violet flame. L. J. S.

**Estimation of Potassium as Perchlorate.** By F. S. SHIVER (*J. Amer. Chem. Soc.*, 1899, 21, 33—42).—The author has investigated the perchlorate method of estimating potash, and finds that the modification of Caspari's method (*Abstr.*, 1893, ii, 390), proposed by Kreider (*Abstr.*, 1895, ii, 414), in which the perchlorate is filtered through a Gooch crucible, gives good results. T. H. P.

**Estimation of the Lime, Potash, and Phosphoric Acid Probably Available for Ensuing Crops (on Hawaiian Soils).** By WALTER MAXWELL (*J. Amer. Chem. Soc.*, 1899, 21, 415—417).—The author considers that in the analysis of soils, the solvent employed should be similar to those operating in the natural processes of soil disintegration and plant food preparation. Such a solvent is aspartic acid, which dissolves phosphoric acid, lime, potash, and other bases from the soil in almost the same proportions as those found in the "waters of discharge," and in which they are removed by cropping. The method employed is as follows. To 200 grams of air dried soil, 1 litre of 1 per cent. aspartic acid solution is added, and the mixture gently shaken every quarter of an hour for 9 hours. After standing for 24 hours, the liquid is filtered, and a definite volume of the filtrate evaporated to dryness and gently ignited to destroy organic matter. The residue is twice moistened with hydrochloric acid, evaporated to

dryness, dissolved in water, and filtered. The iron and aluminium are removed by precipitation with ammonia, and the lime and potash determined as usual. The phosphoric acid in the ammonia precipitate is estimated in the ordinary way.

T. H. P.

**Estimation of Zinc.** By A. C. LANGMUIR (*J. Amer. Chem. Soc.*, 1899, 21, 115—119).—For the estimation of zinc, the separated sulphide is redissolved in hydrochloric acid, the solution is boiled down with nitric acid, and the nitrate is converted into oxide by strong ignition in a weighed platinum dish. The recommendation is made that the zinc sulphide precipitate should not be washed, but a correction made, subsequently if the zinc oxide is found to contain traces of iron, calcium, or magnesium, or if any sulphate remains after ignition.

For the analysis of alloys containing copper, tin, lead, iron, and zinc, the nitric acid solution is evaporated to dryness and the tin is separated by redissolving in nitric acid; the copper and lead are then separated by electrolysis of the solution, which should contain 5 to 10 c.c. of concentrated nitric acid in 150 to 200 c.c. of water; the solution is then evaporated to dryness and ignited in a weighed platinum dish; if iron or nickel is present, it is estimated subsequently, and the values obtained are deducted from the weight of the zinc oxide. For the estimation of zinc in impure spelter, the lead is separated by electrolysis of the nitric acid solution, and the zinc nitrate is converted into oxide as before; the iron is then estimated by titration, and a corresponding correction made in the weight of the zinc oxide; if cadmium and arsenic are present, it is necessary to effect a separation by means of hydrogen sulphide.

T. M. L.

**Estimation of Zinc in Ores containing Aluminium.** By EDMUND JENSCH (*Zeit. angew. Chem.*, 1899, 465—467).—It is well known that in separating zinc from iron, manganese, or aluminium by means of ammonia, the precipitate retains zinc which may, however, be recovered by dissolving in acid and reprecipitating with ammonia. It is now shown that in the presence of much alumina, the process of redissolving and reprecipitating should be repeated not less than four times in order to extract all the zinc.

L. DE K.

**Colorimetric Estimation of Copper.** By MAURICE LUCAS (*Bull. Soc. Chim.*, 1898, [iii], 19, 815—817).—Objection is taken to the use of ammonium nitrate and to other modifications recommended by Jagnaux (*Analyse chimique*, 451) in the estimation of small quantities of copper by the depth of the colour produced on adding potassium ferrocyanide solution, the evaporation of the hydrochloric acid solution to dryness, and dissolution of the residue in water being considered preferable. The process is suitable for the estimation of the copper deposited electrolytically from solutions of iron and steel, and also for the estimation of oxygen in commercial copper. For the latter purpose, the metal is treated with silver nitrate solution, the precipitate boiled with 5 per cent. hydrochloric acid to dissolve the basic copper nitrate, and the copper subsequently deposited by electrolysis and estimated colorimetrically.

N. L.

**Separation of Copper from Antimony.** By MAURICE LUCAS (*Bull. Soc. Chim.*, 1898, [iii], 19, 817—819).—The mixed sulphides of the metals are treated with sodium sulphide solution, the liquid warmed with hydrogen peroxide to destroy polysulphides, and submitted to repeated electrolysis by Classen's method, until deposits consisting only of copper are produced. The metallic deposits are dissolved in nitric acid, the solution mixed with ammonia and ammonium sulphide, the precipitated copper sulphide separated by filtration, redissolved, and the copper estimated colorimetrically by the method previously described (preceding abstract). The small quantity of copper thus determined is deducted from the total weight of the antimony-copper deposit, and added to that of the copper corresponding with the copper sulphide remaining in the electrolytic cell, which, after the greater part of the sodium sulphide has been destroyed by adding hydrogen peroxide, is collected and estimated in the usual manner. The test analyses quoted are very satisfactory.

N. L.

**Electrolytic Estimation of Lead in the Commercial Metal and in Alloys.** By AUGUSTE HOLLARD (*Bull. Soc. Chim.*, 1898, [iii], 19, 911—915).—Careful study of the conditions which it is necessary to maintain in the accurate estimation of lead has shown that closely adherent deposits of lead peroxide may be obtained by electrolysis for 24 hours with a current of 0.15 ampère between an anode formed by a platinum cone and a cathode consisting of a spiral of platinum wire. The solution, measuring about 350 c.c., should contain 80 c.c. of free nitric acid, and not more than 0.2 gram of lead. In order that the deposit may have exactly the composition  $\text{PbO}_2$ , it is absolutely necessary that it should be dried at  $200^\circ$  for 15 minutes. The process is applicable to the estimation of lead in its alloys with zinc and tin, but not to those containing antimony, the oxide of this metal being deposited along with the lead peroxide. In the presence of copper, as in the analysis of brass and bronze, a part of the oxygen required for the peroxidation of the lead is derived from the copper nitrate present in the solution, and it is therefore necessary to reduce the free nitric acid to 14 c.c. per 350 c.c. of solution, and, at the same time, to increase the current to 0.3 ampère.

N. L.

**Volumetric Estimation of Mercury by Alkaline Arsenite.** By W. FEIT (*Zeit. anal. Chem.*, 1899, 38, 242).—The author claims priority (Abstr., 1889, 927) as regards the method described by Reichard (this vol., ii, 183).

M. J. S.

**Separation of Manganese Oxide, Magnesia, and the Alkaline Earths.** By ANTOINE VILLIERS (*Bull. Soc. Chim.*, 1898, 19, [iii], 710—713).—Notable quantities of these oxides are precipitated when a ferric salt is added to an acetic acid solution of their phosphates, and when a mixture of recently precipitated ferric and calcium phosphates is treated with acetic acid only a portion of the calcium passes into solution. The quantitative separation of phosphoric acid from these oxides by the ferric phosphate method is only possible when the iron is present in considerable excess. The solution under examination is evaporated with hydrochloric acid to remove silicic

acid, and ignited to remove organic substances; this treatment destroys oxalic acid, but when manganese is present, this acid may be oxidised to carbonic anhydride by warming the solution with aqua regia. Phosphoric acid being present, the solution is partially neutralised with ammonia, and the slight precipitate produced is redissolved in the least possible amount of hydrochloric acid. Unless iron is present in sufficient excess, the addition of an alkali acetate produces a precipitate of ferric phosphate; if a turbidity appears, ferric chloride is added until the phosphate is redissolved; the solution should remain clear on adding a further quantity of alkali acetate. The solution is boiled, and if the supernatant liquid retains the colour due to ferric salts, more alkali acetate is added; the ferric phosphate should be filtered as rapidly as possible, otherwise traces of iron will pass into solution owing to the action of atmospheric carbonic anhydride; these are removed by boiling the solution and repeating the filtration. The filtrate, when rendered ammoniacal, yields a precipitate which is added to the preceding, and the whole examined for aluminium and chromium; the final filtrate contains manganese, the metals of the alkaline earths, and magnesium; these are separated by the ordinary methods.

G. T. M.

NOTE.—The author does not include zinc, nickel, or cobalt in this scheme of analysis, because their phosphates remain dissolved, providing that ammonium chloride and ammonia are present in sufficient excess. This condition is one which is not usually realised in practice.

G. T. M.

**Rapid Estimation of Tungsten in Steel.** By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1899, 21, 239—245).—In the estimation of tungsten, the amount of ferric oxide carried down by the tungstic acid is fairly constant and need not be separately estimated; it lies between 0.02 and 0.03 per cent. of the weight of tungsten when the latter is less than 1 per cent. of the steel, and between 0.03 and 0.04 for 1 to 2 per cent. of tungsten in the steel. To ensure accurate results, the solution from which the tungstic acid is filtered should contain as little free acid as possible, and the previous evaporation to dryness and dehydration of the silica should be made in hydrochloric and not in nitric acid solution. The phosphorus in tungsten steel may be estimated in the usual way if the amount is small, provided the yellow precipitate is not left for more than  $2\frac{1}{2}$  hours.

T. M. L.

**Analysis of Alloys Containing Tin and Antimony.** By A. FRAENKEL (*Chem. Centr.*, 1899, i, 232; from *Mitt. Technol. Gewerb.-Mus., Wien*, [ii], 8, 334—336).—The following process is suggested for the estimation of tin and antimony in the presence of lead, copper, and even phosphorus. After treatment with nitric acid, the insoluble residue is fused with sodium hydroxide in a silver crucible; the fused mass is extracted with water, one-third of its volume of alcohol is added to the extract, and after 24 hours the liquid containing the tin, and also any lead and phosphorus, is filtered from the insoluble residue, consisting of sodium metantimoniate and copper oxide (A). The filtrate is treated with hydrogen sulphide and the lead collected and weighed as sulphide; on adding acetic acid to the filtrate, tin

bisulphide is precipitated and is converted, as usual, into dioxide and weighed; the phosphoric acid remains in solution and is estimated as usual. The insoluble matter (A) is dissolved in hydrochloric and tartaric acids, and after passing hydrogen sulphide, the copper and antimony sulphides are separated by means of ammonium sulphide.

The nitric acid solution is analysed by the ordinary process, the lead, copper, and antimony precipitates being respectively united with those recovered from the insoluble residue.

L. DE K.

**Analysis of Antimony Sulphide.** By KITZING (*Chem. Centr.*, 1899, i, 59; from *Zeit. öffentl. Chem.*, 4, 830—833).—The following process is recommended for the analysis of *sulphur auratum*. *Total Sulphur.* Water is estimated by drying at 105—110°. 0.5 gram of the dried sample is mixed with 5 grams of tartaric acid and oxidised first with dilute and then with strong nitric acid; after 24 hours, a few c.c. of bromine are added and the mixture left overnight; if any unoxidised sulphur is then visible, a few crystals of iodine are added. After removing the bromine and nitric acid by repeated evaporation with hydrochloric acid, the residue is dissolved in hot dilute hydrochloric acid containing some tartaric acid, and the sulphuric acid precipitated as usual by means of barium chloride. *Free Sulphur.* 10 grams of the sample, dried at 105—110°, is extracted for 30 hours with ether in a Soxhlet apparatus, and the insoluble residue dried and weighed. *Antimony.* 0.2 gram of the dried sample is dissolved in a mixture of nitric and tartaric acids, &c., and the metal precipitated by means of hydrogen sulphide; the sulphide is afterwards converted into antimony dioxide by oxidation with fuming nitric acid and subsequent ignition. Owing to defective washing, the sample may contain some salts soluble in hot water; these may be estimated in the usual way.

L. DE K.

**Lacmoid, Phenacetolin, and Erythrosin as Indicators in the Determination of the Alkalinity of Water by Hehner's Method.** By JOSEPH W. ELLMS (*J. Amer. Chem. Soc.*, 1899, 21, 359—369).—By comparative titration of solutions of calcium and magnesium carbonates of known strength, using as indicators lacmoid, phenacetolin, and erythrosin, it is found that almost equally good results are obtained in each case, but that if uniformity within very narrow limits is required, the preference should be given to erythrosin.

T. H. P.

**Estimation of the Acidity of Urine.** By GEORGES DENIGES (*Bull. Soc. Chim.*, 1898, [iii], 19, 820—822).—The method for estimating the acidity of urine recently described by Lepierre (*Abstr.*, 1898, ii, 652), is practically identical with a method, based on the observations of Maly, which the author described in a thesis published in 1884, and which he has subsequently improved. The following method of procedure is recommended. 20 c.c. of urine are mixed with 20 c.c. of *N*/10 sodium or potassium hydroxides, and 10 c.c. of a 10 per cent. solution of barium chloride and the liquid boiled, cooled, made up to 100 c.c., and filtered. 50 c.c. of the filtrate are then mixed with 10 c.c. of *N*/10 hydrochloric acid and the liquid titrated with *N*/10 soda, using phenolphthalein as indicator.

N. L.

**Acidity of Urine.** By E. LÉPINOIS (*Bull. Soc. Chim.*, 1898, [iii], 19, 822. Compare preceding abstract).—It is pointed out that the process for the estimation of the acidity of urine described by Lepierre is the same as that devised by Maly, and modified by Guichard and by Drouin. The process is, moreover, inexact, as has been shown by Lieblein (*Abstr.*, 1895, ii, 55) and by the author (*Abstr.*, 1896, ii, 397).  
N. L.

**Acidity of Urine.** By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1898, [ii], 19, 927—933. Compare preceding abstracts).—The author makes no claim to originality as regards the Maly-Denigès process for the estimation of the acidity of urine, and describes experiments with a solution of sodium dihydrogen phosphate which show that the best results are obtained by working in the cold, as originally proposed. If the liquid is boiled with alkali and barium chloride solution, as suggested by Denigès, more basic phosphate is precipitated than is the case at the ordinary temperature; the precipitate appears to have the composition  $(\text{PO}_4)_2\text{Ba}_3\cdot\text{BaO}$ . A paper recently published by Lépinos (*Arch. méd. exp. et anat. path.*, 1898) is also criticised, and it is pointed out that much of the confusion which has arisen on the subject of the acidity of urine is the result of not clearly distinguishing between the absolute acidity, as measured by the number of replaceable hydrogen atoms, and the relative acidity, as determined by titration without the use of barium chloride, which depends on the nature of the indicator employed.  
N. L.

**Acidity of Urine.** By H. IMBERT and A. ASTRUC (*Bull. Soc. Chim.*, 1898, [iii], 19, 1016—1017).—Referring to the discussion between Denigès, Lépinos, and Lepierre on the acidity of urine (preceding abstracts), the authors express their full agreement with Lepierre's views on this subject, but they prefer to use calcium chloride instead of barium chloride for the precipitation of the phosphoric acid, since, as they have previously shown (*Soc. Biol.*, 1897; *J. Pharm.*, 1898), more accurate results are thus obtained.  
N. L.

**Volumetric Estimation of Hydrogen, Methane, and Nitrogen in Mixtures of Gases by Fractional Combustion with Copper Oxide.** By ED. JAEGER (*Chem. Centr.*, 1899, i, 59—60; from *J. f. Gasbel*, 41, 764—766).—If a mixture of these three gases is left for some time in contact with copper oxide heated at  $250^\circ$ , the hydrogen is oxidised, whilst the methane is not affected. After noting the contraction, representing hydrogen, the gas is passed over red hot copper oxide, and the contraction, after absorbing the carbonic anhydride by means of aqueous potash, represents the volume of the methane.

The essential feature of the apparatus used by the author is a combustion tube placed between a Bunte's burette and a Hempel pipette. This tube is made from a glass tube 6 cm. long and 1 cm. wide by drawing out one end to a capillary tube to be connected with the burette, whilst the other end is drawn out so as to form a tube of 0.5 cm. width and 4.5 cm. length to be connected with the pipette. The tube is filled with powdered copper oxide, a small granule of the oxide being placed at the capillary end of the tube; both ends are also closed



with a loose plug of asbestos. The tube is heated in a specially constructed furnace fitted with a thermometer. A blank experiment should be made once for all to allow for the volume of air contained in the tube, the oxygen of which also takes part in the combustion. The slight error caused by the fact that the reduced copper occupies a less volume than the copper oxide may be neglected. L. DE K.

**Absorption of Methane and Ethane by Fuming Sulphuric Acid.** By R. A. WORSTALL (*J. Amer. Chem. Soc.*, 1899, 21, 245—250).—Contrary to the usual statement, methane and ethane are absorbed by fuming sulphuric acid. With a specimen of methane from methylic iodide, an absorption of 45.40 per cent. occurred in 11 days, and after 3 months 71.7 per cent. was absorbed, the acid becoming cherry-red in colour; with methane from natural gas, 24.3 per cent. was absorbed in 17 days, and 30.7 per cent. after 3 months. With a specimen of ethane from ethylic iodide, 70.5 per cent. was absorbed in 15 days, and 88.3 per cent. after 3 months. The absorption of methane in one hour is only slight, but in the case of ethane it might be sufficient to affect the analysis, and 15 minutes is probably the maximum of safety. T. M. L.

**Detection and Estimation of Bromoform.** By A. RICHAUD (*J. Pharm.*, 1899, [vi], 5, 232—236).—An aqueous solution of potash is added to the liquid to be tested for bromoform and the mixture heated for 1½ hours in a reflux apparatus, the potassium bromide formed then being tested for, or estimated in, the usual way. If the liquid contains organic matter, it is first distilled, when the whole of the bromoform passes over with the first 75—100 c.c. of the distillate. The distillate is then heated with aqueous potash, evaporated to dryness, and carefully calcined to destroy any organic matter which may have distilled over. H. R. LE S.

**Estimation of Ferrocyanides in Spent Gas-Purifying Material.** By EDUARD DONATH and B. M. MARGOSCHES (*Zeit. angew. Chem.*, 1899, 345—347).—Fifty grams of the sample are washed with carbon bisulphide to remove free sulphur and the greater part of the tarry matters. When dry, the mass is digested in a litre flask with 150 c.c. of 15 per cent. aqueous caustic potash to decompose the ferrocyanides and afterwards diluted with water to 1030 c.c., the volume of liquid then being practically one litre. An aliquot part of the filtrate is taken, and the iron contained in the ferrocyanogen radicle is precipitated by boiling with an alkaline solution of bromine (80 grams of sodium hydroxide is dissolved in water; after cooling, it is made up to a litre and 20 c.c. of bromine added). The iron is precipitated as a fine cinnabar-red compound of doubtful composition; it must therefore be dissolved in dilute sulphuric acid, reduced with zinc, and titrated with permanganate, or it may be dissolved in hydrochloric acid, reprecipitated with ammonia, and weighed as oxide.

Instead of using brominated soda, potassium permanganate may be used, but the iron precipitate is then largely mixed with manganese, which complicates the analysis. One part of the metallic iron corresponds with 7.5476 parts of crystallised potassium ferrocyanide.

L. DE K.

**Detection of Ethylic Alcohol in Ether.** By LASSAR-COHN (*Zeit. anal. Chem.*, 1899, 38, 251; from *Sddeutsch Apothek.-Zeit.*).—The ether is shaken with water, the aqueous layer removed, and freed from dissolved ether by careful warming. The alcohol remaining in the water is oxidised by manganese dioxide and sulphuric acid, the aldehyde produced is distilled off, and the distillate tested with Nessler's reagent. For quantitative estimation, the aqueous layer is warmed to 60°, and the ether expelled completely by a current of hydrogen; the liquid is then distilled and the distillate received in 10 c.c. of *N*/700 iodine solution. This liquid is then shaken with 10 c.c. of normal potassium hydroxide solution, when iodoform is produced, and the excess of iodine is titrated after acidifying with hydrochloric acid. M. J. S.

**Analysis of Dynamite and Gelatin-Dynamite.** By FRANK W. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 425—431).—(a) Dynamite. The moisture is determined by drying in a desiccator over sulphuric acid for five days. A portion is extracted with ether until tissue paper, dipped in the ether and dried, no longer tastes of nitroglycerol; the residue, after drying at 80° for 2 or 3 hours, is weighed, the loss of weight *minus* the moisture giving the nitroglycerol. Next, the mass is extracted with cold water, which is finally displaced by acetone, so as to dry the residue without affecting any starch present. The loss in weight by the water extraction represents sodium nitrate. The remaining mass is ignited until free from carbon, the loss of weight giving the wood-pulp, flour, bran, &c. If much ash is present, it is extracted with hydrochloric acid. The loss on ignition, less the loss by the acid extraction, is called wood-pulp, and the basic magnesium carbonate is taken as twice the loss of weight by the acid treatment. The analysis may be checked by measuring in the nitrometer the volume of nitric oxide evolved by a known weight of the dynamite, and then taking separately the corresponding quantities of sodium nitrate and nitroglycerol, and measuring in each case the nitric oxide. Concordance in these measurements shows that the ether extracts nothing but nitroglycerol, and the water only sodium nitrate.

(b) Gelatin-Dynamite. The moisture is found as in (a). About 15 grams of the dynamite are extracted with chloroform in a Soxhlet apparatus, the loss in weight being nitroglycerol, sulphur, and resin. The residue is extracted with water to remove sodium nitrate and then with acetone, which dissolves out the guncotton. The wood-pulp and earthy absorbents remaining are treated as described under (a). The chloroform solution is evaporated until nearly all the solvent is removed, glacial acetic acid being then added, and the precipitated sulphur transferred to a Gooch crucible and treated with strong alcohol to remove the resin. The nitroglycerol is determined by repeatedly treating a portion of the dynamite with cold ether, the ethereal solution being allowed to evaporate spontaneously. The residue is washed into the nitrometer with acetic acid, and the nitroglycerol calculated from the volume of nitric oxide obtained. The resin may be estimated by difference. T. H. P.

**Estimation of Dextrose.** By ADOLF BICKEL (*Pflüger's Archiv*, 1899, 75, 248—264).—In estimating dextrose, any boiling or concentration of aqueous solutions may lead to loss of sugar if the solution is alkaline; the reaction must therefore be acid, when no change occurs in dilute solutions. W. D. H.

**Estimation of Dextrose by Lehmann's Method.** By LÉON MAQUENNE (*Bull. Soc. Chim.*, 1898, [iii], 19, 926—927. Compare *Abstr.*, 1898, ii, 264, 355).—In the estimation of sugar according to the method proposed by Lehmann, and more recently by Riegler, which consists in titrating by means of potassium iodide and thiosulphate the excess of copper remaining after treatment with Fehling's solution, it is found that the removal of the precipitated cuprous oxide by filtration may be omitted, thus rendering the process more rapid, without loss of accuracy. The following modified method of procedure is recommended. A quantity of the sugar solution containing less than 0.05 gram of glucose is added to 10 c.c. of Fehling's solution, and the liquid diluted with water to 30 c.c., boiled for 2 minutes, rapidly cooled, and mixed with 20 c.c. of sulphuric acid (50 per cent. by volume), and 10 c.c. of 10 per cent. potassium iodide solution. The solution is then immediately titrated with thiosulphate, using starch as an indicator, and the volume used deducted from that required in a blank experiment carried out in a similar manner with 10 c.c. of Fehling's solution. A table is given in the paper, showing the weight of inverted cane sugar corresponding with different volumes of 2 per cent. thiosulphate. N. L.

**Estimation of Carbohydrates.** By FRANK W. TRAPHAGEN and W. M. COBLEIGH (*J. Amer. Chem. Soc.*, 1899, 21, 369—373).—100 c.c. of Fehling's solution, diluted with an equal volume of water, is heated on a water-bath and treated with the solution to be tested in the ordinary way. The precipitated cuprous oxide is collected and washed on an asbestos filter, the top layer of which, with the cuprous oxide, is removed, well stirred with water, and treated with 50 c.c. of a saturated solution of ferric sulphate in 20 per cent. sulphuric acid. When dissolved, the liquid is filtered through the same asbestos filter to remove any traces of cuprous oxide, and is then titrated with permanganate. The amounts of cane sugar and of starch corresponding with each c.c. of the permanganate solution must be previously determined by titrating with pure cane sugar and with a carefully analysed starch. The weight of cuprous oxide precipitated should be about the same in all cases, the method then giving reliable results. Experiments show that there is no danger of the cuprous oxide being oxidised, even if left on the filter all night, nor of its dissolution if left in contact with the alkaline liquid. T. H. P.

**Estimation of Glycogen.** By JOS. WEIDENBAUM (*Pflüger's Archiv*, 1899, 75, 113—119). By EDUARD PFLÜGER (*ibid.*, 120—247).—The methods at present in use for the estimation of glycogen are subjected to experimental criticism; Külz's method especially was examined, and considerable loss of glycogen was found to occur in its various stages. Some modifications are suggested, but even then the loss amounts to 12 per cent. W. D. H.

**Detection of Caramel in Spirits and Vinegar.** By CHARLES A. CRAMPTON and F. D. SIMONS (*J. Amer. Chem. Soc.*, 1899, 21, 355—358).—Spirits artificially coloured with caramel can be distinguished from those the colour of which is derived from long storage in cask by keeping the liquor for some time in contact with a definite quantity of Fuller's earth, and determining, by means of the tintometer, the percentage of colour removed; much more of the artificial colouring matter is absorbed than of the natural. Thus, for 40 samples of naturally coloured spirits, the mean percentage of colour removed was 14.6, the limits being 25.0 and 8.3 per cent.; whilst 18 samples of artificially coloured spirits gave a mean of 44.7 and a maximum and minimum of 54.1 and 40.0 per cent. respectively of colour removed. The test probably applies also to vinegars. T. H. P.

[**Discrimination of Amber from Copal. Test for Arsenic in Carpets.**] By OSCAR RÖSSLER (*Arch. Pharm.*, 1899, 237, 239—240).—When a fragment of amber is heated in an ignition tube, the vapours evolved blacken lead acetate paper; this is not the case with copal. Judged by this test, the trinkets found at Troy and Mycenae are found to be carved out of amber, and not out of fossil copal.

Green carpets are coming into fashion again in Germany in consequence of the revival of the Empire style. They may be tested for arsenic by rolling up a fragment in a coil of platinum foil and heating it in the upper oxidising zone of the Bunsen flame under a glazed porcelain basin filled with cold water. A drop of silver nitrate solution is then drawn across the underside of the basin by means of a glass rod, and air is blown on to it after first passing over a glass stopper moistened with ammonia; a yellow precipitate indicates the presence of arsenic in the carpet. C. F. B.

**Estimation of Oil and Spirit of Mustard.** By BRUNO GRÜTZNER (*Arch. Pharm.*, 1899, 237, 185—189).—About 0.2 gram of the oil is dissolved in 10 c.c. of alcohol (or about 10 grams of the spirit are taken), mixed with 3.5 grams of ammonia and allowed to remain overnight in a stoppered vessel; the thiocarbimide is thus converted into the thiocarbamide. The whole is then rinsed into a beaker and heated on the water-bath until the ammonia has volatilised; a clear solution of sodium peroxide, free from sulphate, is added to the cooled liquid, which is then heated until no more oxygen is evolved, acidified with hydrochloric acid, and precipitated with barium chloride, the barium sulphate being weighed. From experiments with several samples, it was found that 1 gram of barium sulphate corresponds with 0.48021 gram of the pure natural oil.

The sulphate may also be precipitated with a weighed excess of barium chloride, or better, with a measured excess of  $N/2$  barium chloride solution, the excess being estimated volumetrically. The liquid and precipitate are diluted to a total volume of 500 c.c., 250 c.c. are precipitated with sodium carbonate, the precipitate of barium carbonate (mixed with sulphate) is washed carefully, treated with a measured excess of  $N/2$  hydrochloric acid and boiled, the excess of acid being then titrated with  $N/2$  potassium hydroxide and phenol

phthalein. Of the barium chloride solution, 1 c.c. corresponds with 0.02797 gram of the natural oil.

A specimen of artificial oil was found to contain only 0.4 per cent. more sulphur than the natural oil (28.6 per cent.). This oil boiled at 148—149.5°, had a sp. gr. 1.02 at 15°, and satisfied the requirements of the German pharmacopœia. It is thus impossible to distinguish in this way the artificial from the natural oil. C. F. B.

**Preparation of a Titrated Solution of Acetaldehyde.** By XAVIER ROCQUES (*Chem. Centr.*, 1899, i, 60—61; from *Ann. Chim. anal. appl.*, 3, 365).—1.386 grams of aldehyde-ammonia which have been thoroughly extracted with ether and dried, are placed in a 100 c.c. measuring flask and dissolved in 50 c.c. of 96 per cent. alcohol; 22.7 c.c. of normal (alcoholic) sulphuric acid are added, which soon causes a precipitate of ammonium sulphate; the measure is filled to the mark with alcohol, an extra 0.8 c.c. being added to compensate for the volume occupied by the precipitate. After remaining overnight, the liquid, which contains exactly 1 per cent. of aldehyde, is filtered. The solution may then be further diluted with water or proof-spirit, so as to contain exactly 0.050 gram of aldehyde per litre.

L. DE K.

**Separation and Estimation of Coumarin and Vanillin in Flavouring Extracts.** By WILLIAM H. HESS and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1899, 21, 256—259).—The alcohol is removed by heating at 80°, lead acetate is then added so long as a precipitate forms, and the filtered solution is extracted with ether. The vanillin in the ethereal extract is extracted with ammonia, and after neutralising with 10 per cent. hydrochloric acid and drying below 55°, is taken up with light petroleum and evaporated in a weighed dish. The coumarin is similarly separated by evaporating the ethereal solution below 45°, extracting with light petroleum, and evaporating in a weighed dish. The vanillin and coumarin are identified by their melting points. T. M. L.

**Estimation of Acetic Acid in Commercial Acetates, and the Separation of Acetic, Propionic, Butyric, and Formic Acids.** By K. R. HABERLAND (*Zeit. anal. Chem.*, 1899, 38, 217—226).—The method for the estimation of acetic acid in calcium acetate adopted by the meeting of Industrial Chemists at Mombach is as follows:—About 10 grains of the pulverised substance are mixed with 50 c.c. of water in a 300 c.c. flask, and then treated with 11 c.c. of hydrochloric acid of sp. gr. 1.124. The mixture is distilled until the residue is syrupy; 50—60 c.c. of warm water added and the distillation again carried to dryness. In one-fifth of the distillate, the total acids are titrated by normal soda and phenolphthalein, and in one-tenth the hydrochloric acid is estimated by adding 15 c.c. of pure nitric acid and an excess of *N*/10 silver nitrate, and titrating the excess of silver in one-half of the filtrate by ammonium thiocyanate. The author confirms the accuracy of this method by proof analyses.

To estimate the four homologous acids in crude acetate, the substance is distilled with phosphoric acid and the distillate evaporated

with lead oxide; the residue is dissolved in cold water and the solution heated to boiling. In consequence of its insolubility in boiling water, basic lead propionate is precipitated, whilst the other lead salts remain in solution and are separated by filtration. The filtrate is treated with sulphuric acid, evaporated to dryness with excess of zinc oxide, and the mass is then treated with a large volume of absolute alcohol. Zinc formate is completely insoluble in this liquid, and remains on the filter with the lead sulphate. The alcoholic filtrate is evaporated to dryness and distilled with phosphoric acid. The butyric and acetic acids may then be separated by either of two processes. They may be treated with silver carbonate and the aqueous solution of the silver salts evaporated on the water-bath, when, in consequence of the considerably lower solubility of silver butyrate, that salt crystallises out with almost quantitative completeness, leaving the silver acetate in solution. The other method is to convert the two acids into their amylic salts by cohobation with amylic chloride and a little 96 per cent. alcohol, and after distilling off the alcohol and the excess of amylic chloride at  $100^{\circ}$  to separate the salts by fractional distillation. A proof analysis gave numbers agreeing very closely with the amounts of the four acids employed.

It is incidentally shown that calcium acetate cannot be completely dehydrated at any temperature up to that at which it decomposes.  
M. J. S.

**Detection of Salicylic and Benzoic Acids in Milk.** By G. BREUSTEDT (*Arch. Pharm.*, 1899, 237, 170—172).—25 c.c. of milk are mixed with 25 c.c. of water and 10 c.c. of Fehling's copper sulphate solution, about 2.5 c.c. of *N*-potash added, so that the liquid remains still perceptibly alkaline, and the mixture warmed for a little while in the water-bath, and filtered from copper caseinate and fat. The filtrate is mixed with a few drops of dilute hydrochloric acid, and shaken with ether, the ethereal extract being evaporated. In the residue, salicylic acid can be detected by the violet coloration with dilute ferric chloride solution; benzoic acid, by the brown flakes formed when the residue is dissolved in a little water and boiled with ferric chloride; or, in the presence of salicylic acid, by adding two drops of dilute formic acid and then excess of milk of lime, evaporating, and heating the residue in an ignition tube, when a smell of benzaldehyde is noticed. Salicylic acid can be detected still more easily by heating 10 c.c. of milk with 10 c.c. of fuming hydrochloric acid until a red coloration appears, cooling, shaking with 20 c.c. of ether, evaporating the ethereal extract, shaking the residue vigorously with a little hot water, filtering, and adding ferric chloride to the filtrate.  
C. F. B.

**Analysis of Condensed Milk.** By F. S. HYDE (*J. Amer. Chem. Soc.*, 1899, 21, 439—444).—The whole contents of a tin of the milk are mixed until of the same consistency throughout and a stock solution prepared by mixing 25 grams of the milk with 75 grams of water. The total solids are found by evaporating five grams of the solution and drying the residue at  $100^{\circ}$ . The percentage of fat is obtained by absorbing a known weight of the solution by an Adams'

coil, which is dried and extracted with ether in a Soxhlet apparatus. The milk sugar is determined by titration with Fehling's solution. The cane sugar is obtained by boiling the stock solution with citric acid, which inverts the cane sugar but not the milk sugar; the solution is cooled, neutralised with potassium hydroxide solution, made up to a known volume, and titrated with Fehling's solution. The reduction corresponds with a certain amount of cane sugar from which must be subtracted the milk sugar in terms of cane sugar. The proportion of milk solids is found by deducting the cane sugar from the total solids, and the percentage of water by subtracting the percentage of total solids from 100. The difference between the milk solids and the sum of milk sugar and fat represents casein, albumin, and salts. The ash is obtained in the usual way by ignition of the total solids. The 'degree of condensation' is rather a vague quantity, and is usually taken as the percentage of milk solids divided by 12.5, which is the average for cows' milk.

T. H. P.

**The Heat of Bromination Test for Oils.** By AUGUSTUS H. GILL and ISRAEL HATCH, jun. (*J. Amer. Chem. Soc.*, 1899, 21, 27—29).—This test is carried out in a calorimeter consisting of a flat-bottomed glass tube which is held in a beaker by means of a cork, a protecting air-jacket being thus produced, further insulation being obtained by arranging the beaker inside a larger one, and filling the space between with cotton waste. 5 c.c. of a 20 per cent. solution of the oil in carbon tetrachloride are run into the calorimeter and the temperature read off when constant. 5 c.c. of a solution of 1 volume of bromine in 4 volumes of carbon tetrachloride are then allowed to flow down the sides of the calorimeter and mix with the oil, the highest temperature shown by the thermometer being noted. To make the results given by different calorimeters comparable, sublimed camphor is used as a standard; on dissolving 7.5 grams of this substance in carbon tetrachloride and brominating it, a mean rise in temperature of  $4.2^{\circ}$  is obtained. Then, for each oil examined, the rise of temperature on bromination divided by 4.2 gives the specific temperature reaction, which on multiplication by an empirical factor (the mean for a number of oils of the iodine number divided by the specific temperature reaction), gives the iodine value. The method gives good results except in the case of hydrocarbon oils.

T. H. P.

**Constants of American Linseed Oil.** By AUGUSTUS H. GILL and AUGUSTUS C. LAMB (*J. Amer. Chem. Soc.*, 1899, 21, 29—30).—The authors have determined the constants for a number of specimens of pure American linseed oils and of menhaden oil, which is used both as a substitute and as an adulterant for linseed oil. The determinations include specific gravity, Valenta test, Maumené test, iodine absorption in 4 and in 18 hours, and a drying test. The Maumené and iodine numbers obtained are respectively about 10 and 4 per cent. lower than the usually accepted values. The effect of the menhaden oil is to raise the Maumené number, to lower the iodine value, and to retard the drying of the oil. Contrary to the statement of Dieterich (*Jour. Soc. Chem. Ind.*, 1893, 381), the iodine value is not generally appreciably increased by 18 hours standing.

T. H. P.

**Analysis of Sod Oil.** By ERASTUS HOPKINS, D. L. COBURN, and EDWARD SPILLER (*J. Amer. Chem. Soc.*, 1899, 21, 291—300).—Sod oil or dégras is the waste fat obtained in the chamoising process and is used for currying purposes, that is, dressing bark-tanned leather; analyses of 12 samples are given. The moisture is determined by absorbing the oil with filter papers and drawing air over it at 100°, and ranges from 1 to 40 per cent. of the oil. The oil is then extracted in a Soxhlet apparatus with light petroleum boiling at 40°, which dissolves from 58 to 96 per cent. of the oil; the soap is next extracted with absolute alcohol, and amounts to 0.7 to 8.8 of the oil; the insoluble residue, after deducting the weight of ash, represents the quantity of hide fragments, 0.15 to 3 per cent., in the oil. The quantity of ash is large, owing to the extraction by the oil of the ash of the leather, and is especially rich in calcium salts from the 'liming' of the leather; the quantity varies from 0.05 to 1.04 per cent. The 'dégras former,' which is regarded as the valuable constituent of the oil, is readily saponified; the soap is precipitated by an excess of salt, and acidified with hydrochloric acid, the "dégras former" which separates is then washed with water and light petroleum, dissolved in absolute alcohol, and evaporated in a weighed dish; it is thus obtained as a resinous substance melting at 65—67°, and amounts to 1 to 26 per cent. of the dry oil. Values are also given for the free mineral acid, the free fatty acid, the quantity of ethereal salts, the Reichert-Meissl number, the iodine number, the non-saponifiable matter and its iodine number, each value being calculated for the original oil, the dry oil, and the oil soluble in light petroleum. The wide variation in properties is due to the fact that a number of different oils are used for the manufacture of sod oil, the two principal ones being menhaden and cod oils.

T. M. L.

**Estimation of Alkaloids by Iodine Solution.** By KARL KIPPENBERGER (*Zeit. anal. Chem.*, 1899, 38, 230—236).—In support of his view that the formation of the periodides of the alkaloids does not take place in accordance with the equation  $\text{Alk}, \text{HCl} + \text{KI} + \text{I}_2 = \text{Alk}, \text{HI}, \text{I}_2 + \text{KCl}$  (Abstr., 1896, ii, 282, 682), but that the hydrogen iodide in the product is, at least in part, derived from the decomposition of water by the free iodine, the author states that the periodide of narcotine can be produced by the action of iodine on narcotine hydrochloride in the absence of an alkali iodide. He, however, practically abandons his earlier contention that the conditions of the reaction can be so arranged as to involve the consumption of a uniform molecular proportion of iodine, and insists on the necessity of standardising the iodine solution in each case by means of weighed amounts of the special alkaloid to be estimated.

M. J. S.

**The Volumetric Estimation of Alkaloids.** By O. LINDE (*Arch. Pharm.*, 1899, 237, 172—185).—This paper is the first instalment of an account of the various volumetric methods employed for the estimation of alkaloids. General methods are first discussed, and amongst these in the first place the method of precipitation with potassium mercuriodide solution ("Mayer's reagent"). It is pointed out that the precipitate formed has no definite composition; that an



allowance has to be made for its solubility; that the end point of the reaction is affected by the presence of acid (sulphuric), and also by the concentration of the alkaloid in the solution titrated; moreover, that other substances contained in extracts of plants, beside the alkaloids, are precipitated by the mercuriodide solution. The methods of precipitation with phosphomolybdate and with mercuric chloride solutions are then discussed, and are found to be open to objections of the same kind.

C. F. B.

**Assay of Nux Vomica.** By EDWARD R. SQUIBB (*J. Amer. Chem. Soc.*, 1899, 21, 351—355).—10 grams of the ground seed are extracted with cold 10 per cent. acetic acid, and the liquid evaporated to dryness in a flat-bottomed capsule on a water-bath. To the dry extract are added 10 c.c. of a mixture of 2 vols. of 91 per cent. alcohol, 1 vol. of 10 per cent. ammonia solution, and 1 vol. of water, and the mixture stirred until complete solution takes place. The liquid is then shaken with 40 c.c. of a mixture of equal volumes of chloroform and ether, allowed to settle, and the chloroform-ether solution separated. This extraction is repeated, twice if necessary, the whole of the liquid being evaporated to dryness in a tared flask. 10 c.c. of decinormal sulphuric acid are run into the flask and when the soluble alkaloids are dissolved, 20 c.c. of hot water and a definite quantity of logwood indicator are added, and the amount of alkaloids present calculated from the volume of decinormal potash necessary to give the liquid a pinkish tint.

T. H. P.

**Valuation of Indigo.** By WILHELM HOLTSCHMIDT (*Zeit. angew. Chem.*, 1899, 451—455; 475—479).—The assay of indigo by the present processes is not satisfactory. In the process of titration with permanganate, a serious error may be caused by secondary actions when the sample of indigo is treated with sulphuric acid (sulphonated) at 85°; but this may be avoided by adopting the author's cold process. 0.5—1 gram of the finely-powdered sample is treated in a test-tube with 10 c.c. of sulphuric acid, containing 40 per cent. of phosphoric anhydride, and the mixture well kneaded with a glass rod; the sulphonation is complete in about two hours, but it is safer to leave the mixture overnight in a desiccator. The solution is now poured into a measuring flask containing enough water to prevent any sensible development of heat, the tube is well rinsed with cold water, and the whole finally made up to 500 or 1000 c.c., filtered quickly, and 25 c.c. of the filtrate titrated with  $N/100$  permanganate as follows: After diluting to about 125 c.c., the permanganate is added at the rate of 2 drops per second until the liquid is of a pale green colour, whilst on stirring, dark clouds are visible; 2 or 4 drops of the permanganate are now added at a time with gentle stirring, so as not to disturb the clouds, and the formation of fresh clouds is noticed. When no more are formed, the operation is finished, and 0.1 or 0.2 c.c. of permanganate is deducted from the total. A paraffin lamp may be used as the source of light for the titration. Donath and Strasser's improvement in the titration process (*Abstr.*, 1895, ii, 300) is approved of by the author. This consists in freeing the sample from indigo-glue and indigo-red by successively digesting with dilute hydrochloric acid and alcohol-ether

mixture before sulphonating. The presence of indigo-brown does not interfere with the subsequent titration with permanganate.

Voeller (Abstr., 1891, 1564) proposed to remove the indigo-brown also by treating the sample already freed from indigo-glue and indigo-red with dilute aqueous potash, and then to estimate the nitrogen in the purified indigotin by Kjeldahl's process. The author approves of this method, but recommends the use of a 1 per cent. solution of potassium hydroxide; too long contact with the alkali must be avoided, as otherwise indigo-brown is actually generated from the indigotin. A large number of analyses have been made and tabulated, showing the amount of nitrogenous matter extracted by the various solvents in use to purify the sample before submitting it to the Kjeldahl process. For convenience of comparison, the nitrogen due to the "glue" has been multiplied by the same factor as the other nitrogen.

Part of the paper is devoted to the technical testing of indigo by the colorimetric method, which, however, often fails to give exact indications owing to differences in shade and to the "wool test," which, although valuable to dyers, gives no indication of the true amount of indigotin.

L. DE K.

Estimation of Albumin. By R. DELAUNAY (*J. Pharm.*, 1899, [vi], 3, 100—101).—The albumin in urine is not always completely precipitated by the addition of acetic acid and subsequent heating; if, however, the urine is previously saturated with sodium sulphate, the precipitation is complete; but it is necessary, before weighing the albumin, to wash it with boiling water until free from sulphates.

H. R. LE S.

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## General and Physical Chemistry.

**Optically Transparent Liquids.** By WALTHER SPRING (*Rec. Trav. Chim.*, 1899, 18, 153—168).—Tyndall has assumed that when a beam of light passes through a gas its path is made evident by the illumination of minute solid or liquid particles present as impurities. Lallemand, however, from experiments with carefully distilled liquids, concluded that the illumination of a fluid medium by light is a specific property of the medium, and that each medium has a certain "coefficient of illumination," dependent on its nature. The author now shows that, although it is impossible to obtain a truly transparent liquid (that is, one which is not rendered luminous by the passage of a beam of light) by distillation or filtration, liquids can be rendered optically pure by means of a current of electricity; on passing, for example, a current through water containing a small quantity of silica or ferric hydroxide in suspension, the suspended matter is deposited at the cathode, and carries with it the minute particles which render the water capable of being illuminated. The same result is also obtained by adding clear lime water to a solution of silicic acid, and leaving the precipitate to subside in a stoppered vessel; on examining the liquid in a beam of light, care being taken that the vessel is not opened, it is found to be perfectly transparent. The subsidence of other gelatinous precipitates, such as the hydroxides of iron, aluminium, and zinc, from water renders the latter non-illuminable; the subsidence of crystalline precipitates, however, such as barium sulphate or calcium oxalate, gives no such result. It thus appears probable that the minute suspended particles can only be removed by being surrounded, during the precipitation, with a heavy, gelatinous envelope. The filtration of water through a layer of a gelatinous precipitate, out of contact with the air, renders it transparent; but if filtered in contact with air, this result is not obtained. The reason why distillation fails to yield transparent liquids is thus made evident.

In the case of organic liquids, the author has not obtained such definite results; the subsidence of gelatinous precipitates from organic liquids is, as a rule, very incomplete, so that optical transparency cannot generally be obtained. It appears probable also, that many organic liquids become luminous on the passage of a beam of light, owing to fluorescence.

The particles which are rendered luminous in water by a beam of light appear to consist largely of organic matter, but luminescence is also due to minute bubbles of gas; this is made clear by the increased illumination which occurs when the pressure in the space above the water is diminished, and by the fact that optically transparent water is rendered luminescent by passing air through it. W. A. D.

**Influence of Elements on the Optical Activity of the Amyl Radicle.** By PAUL WALDEN (*J. pr. Chem.*, 1899, [ii], 59, 470—473).—A claim of priority with regard to Brjuchonenko's work on this subject (this vol., ii, 265). R. H. P.

**Interconversion of Optical Antipodes. IV. and V.** By PAUL WALDEN (*Ber.*, 1899, **32**, 1833—1855; 1855—1864. Compare Abstr., 1896, i, 205; 1898, i, 127, 178).—IV.—When lævorotatory chloro- or bromo-succinic acid is acted on with bases, a mixture of lævo- and dextro-malic acids, in varying proportions, is produced. The sign and the specific rotatory power of the malic acid which is formed when different bases are used is shown in the accompanying table; the values given were determined in presence of a uranium salt, which has the effect of increasing the specific rotatory power of malic acid to  $\pm 460^\circ$  (Abstr., 1898, ii, 149).

Halogen acid.	Hydrolysing agent.	Specific rotatory power of malic acid.
I. <i>l</i> -Chlorosuccinic acid .....	Ag <sub>2</sub> O	$[\alpha]_D = -460^\circ$
<i>l</i> -Bromo- " " .....	H <sub>2</sub> O	-212
<i>l</i> -Bromo- " " .....	TlOH	-203
<i>l</i> -Bromo- " " .....	HgO	-172
<i>l</i> -Bromo- " " .....	Hg <sub>2</sub> O	-130
<i>l</i> -Bromo- " " .....	PdO	-125
II. <i>l</i> -Bromo- " " .....	Tl <sub>2</sub> O <sub>3</sub>	$\pm 0$
III. <i>l</i> -Chloro- " " .....	RbOH	+440
<i>l</i> -Chloro- " " .....	KOH	+425
<i>l</i> -Chloro- " " .....	NH <sub>4</sub> OH	+460
<i>l</i> -Chloro- " " .....	CuO	+330
<i>l</i> -Bromo- " " .....	Cd(OH) <sub>2</sub>	+301
<i>l</i> -Chloro- " " .....	Ba(OH) <sub>2</sub>	+170
<i>l</i> -Chloro- " " .....	Pb(OH) <sub>2</sub>	+170
<i>l</i> -Chloro- " " .....	NaOH	+150
<i>l</i> -Chloro- " " .....	Sn(OH) <sub>2</sub>	+130
<i>l</i> -Chloro- " " .....	LiOH	+100

The rotatory power of lævomalic acid is not altered when a solution in strong potassium hydroxide is kept in the dark during 16 months, and it also remains lævorotatory when boiled with dilute caustic potash during 36 hours, although it is not stated that the magnitude of the specific rotatory power is unaltered. From these experiments, and from similar experiments with inactive malic acid, the conclusion is drawn that no change of rotatory power takes place after the hydrolysis of the halogen-acid. For the most part, it is the stronger bases which bring about a reversal of rotatory power during hydrolysis, but no definite relationship can be traced between the influence of the base and its molecular volume, or the atomic volume of the metallic element, or its position in the periodic system. Alkalis have an optical effect in the opposite direction to that of water, and the formation of mixtures of dextro- and lævo-malic acids by the action of aqueous alkalis may be explained, to some extent, by the opposite influence of the two hydrolysing agents which are present; the effect of mixtures of bases is, however, somewhat irregular, since a mixture of silver oxide and potassium hydroxide gives a lævorotatory malic acid, whilst a mixture of silver oxide and ammonia gives a strongly dextrorotatory acid. The nature of the product is largely influenced by the conditions

under which hydrolysis takes place; thus, lithium hydroxide acting on a solution of lævobromosuccinic acid in methylic alcohol (in which the base is only slightly soluble) gives an inactive acid, whilst in aqueous solution a dextrorotatory acid is formed.

It is suggested that the formation of two optical isomerides in the hydrolysis of active chloro- and bromo-succinic acids is probably due to differences in the mechanism of the reaction, one being a direct substitution of hydroxyl for halogen by the interaction of ions, and the other an indirect action depending on the formation of an intermediate additive product from the base and acid.

In general, it may be said that the strong bases cause a reversal of rotatory power, whilst feeble bases, which tend to form additive compounds, give a malic acid of similar rotatory power, but exceptions occur in the case of copper, cadmium, lead, and tin oxides on the one hand, and thallic hydroxide on the other.

V.—The following actions have been described in the earlier papers :

I. *L*-Malic acid gives *d*-chloro- and bromo-succinic acids by the action of phosphorus pentachloride.

II. *L*-Aspartic acid and *L*-asparagine give *l*-malic acid by the action of nitrous acid.

III. *L*-Aspartic acid and asparagin give *l*-chloro- and bromo-succinic acids by the action of nitric oxide and chlorine or bromine.

IV. *L*-Chloro- and bromo-succinic acids give *l*-malic acid by the action of silver oxide, but *d*-malic by the action of potassium hydroxide.

Natural malic acid is described throughout as 'lævo,' although the free acid is dextrorotatory; the esters, amides, acetyl esters, the esters of methoxy-, ethoxy-, isopropoxy-, and isobutoxy-succinic acid, and the esters of nitromalic acid are lævorotatory, whilst among the derivatives only the chloro- and bromo-succinic esters, prepared by the action of pentachloride and pentabromide of phosphorus, are dextrorotatory. The change of sign on substituting chlorine or bromine for a hydroxyl or similar radicle is of very general occurrence, where the substitution is made directly on an active asymmetric carbon atom, and has been observed in the esters of *l*-mandelic acid, *d*-tartaric acid, *d*-lactic acid, *l*- $\alpha$ -hydroxybutyric acid, *l*-methylpropylcarbinol, *d*-methylethylcarbinol, and *l*-methylethylcarbinol; exceptions are found in the case of *l*-propylene glycol and the chloride of *l*-isobutylic  $\alpha$ -hydroxybutyrate. The action of phosphorus pentachloride and pentabromide is therefore regarded as normal, and dextrorotatory chloro- and bromo-succinic acids are described as 'lævo.' The action of potassium hydroxide and allied bases (the third group in the table) is therefore normal, whilst silver oxide and the first group of bases have an abnormal optical influence, and bring about a change of configuration; the different behaviour of the cyanides, nitrites, cyanates, and sulphites of potassium and silver is quoted as an analogous case, the potassium salts acting directly, and the silver salts forming intermediate additive products.

It is open to question whether asparagine and aspartic acid have the configuration of dextro- or of lævo-malic acid; in the former case, the formation of lævomalic acid by the action of nitrous acid is an abnormal action, whilst in the latter case the formation of chloro-

and bromo-succinic acids by the action of nitric oxide and chlorine or bromine is abnormal.

If, instead of regarding as 'lævo' all acids which are derived directly from lævomalic acid or are converted directly into it, the sign of the rotatory power alone is considered, then optical inversion occurs in the action of phosphorus pentachloride and pentabromide, of nitrosyl chloride and bromide, of nitrous acid, and of potassium hydroxide and the third group of bases, and the only 'normal' action in which no inversion occurs is the hydrolysis by means of silver oxide and the first group of bases.

T. M. L.

**Theory and Application of a New Method of Interference Spectroscopy.** By CH. FABRY and A. PEROT (*Ann. Chim. Phys.*, 1899, [vii], 16, 115—144).—A physical paper, not suitable for abstraction.

G. T. M.

**A Photographic Investigation of the Absorption Spectra of Chlorophyll and its Derivatives in the Violet and Ultra-violet Region of the Spectrum.** By C. A. SCHUNCK (*Proc. Roy. Soc.*, 1898, 63, 389—396).—Tschirch found (*Ber. deut. Bot. Ges.*, 10, 76) that derivatives of chlorophyll show a characteristic absorption band in the ultraviolet region of the spectrum, occupying the same position as a similar band in hæmoglobin derivatives. The author, who has confirmed Tschirch's experiments, has examined a larger number of chlorophyll derivatives, and finds that in all of them there is a characteristic absorption between the solar lines F and M; this, in conjunction with the very similar absorption of hæmoglobin derivatives, is taken as supporting the view that chlorophyll and hæmoglobin have something in common. The chief point in which the author's results differ from those of Tschirch is that the former finds that only some of the derivatives are characterised by the single band; some show two, or even three, bands.

J. C. P.

**Aluminium as an Electrode in Cells for Direct and Alternate Currents.** By ERNEST WILSON (*Proc. Roy. Soc.*, 1898, 63, 329—347).—When a plate of aluminium is made the anode in a cell containing a solution of alum, it offers a great resistance to the passage of a current. Two electrodes, one of aluminium and one of carbon, were immersed in a saturated solution of alum and connected with twenty-two storage cells. When the aluminium was connected with the negative battery pole, the current was 3.6 ampères, and the potential difference between the electrodes was 4.4 volts; when the aluminium was connected with the positive battery pole, the current was zero, and the potential difference about 22 volts. The influence of temperature was found to be considerable, the potential difference in one cell sinking from 30 to 3 volts as the temperature rose from 13.5° to 70°.

A film, formed on the aluminium anode, seems to be the cause of the great resistance; this film, which analysis showed to be basic aluminium sulphate, was found to be a fairly high, although unstable, insulator. Two aluminium plates, with their films, were immersed in saturated and unsaturated solutions of sodium, ammonium, and

potassium alums, and it was found that, with suitable current density and temperature, such a system made an efficient condenser.

It was thought that aluminium-carbon cells might serve to rectify an alternate current, but this expectation was not fulfilled with the cells and frequencies used. It was shown, however, that the half-period during which the electricity traversing the circuit was a minimum was that in which the aluminium acted as anode.

J. C. P.

**Electromotive Efficiency of Carbonic Oxide.** By VICTOR HOEPER (*Zeit. anorg. Chem.*, 1899, 20, 419—451).—By combination with the normal electrode  $\text{KCl} \mid \text{HgCl} \mid \text{Hg}$ , the potential difference between platinum charged with carbonic oxide and a normal solution of hydrochloric acid is found to be  $-0.70$  to  $-0.60$  volt. When oxygen or air is passed in instead of carbonic oxide, the value is  $-1.1$  to  $-0.9$  volt. These relative values agree with the E.M.F. of the combination  $\text{Pt} \mid \text{CO} \mid \text{HCl} \mid \text{HgCl} \mid \text{Hg} \mid \text{HgCl} \mid \text{HCl} \mid \text{O} \mid \text{Pt}$ , which is  $0.45$  volt; when carbon is substituted for platinum, a similar value is obtained. The effect of mixing air and carbonic anhydride with the carbonic oxide is determined, and from a theoretical discussion it appears probable that carbonic oxide is not indifferent to the oxygen, but unites with it largely to form carbonic anhydride.

The potential difference between platinum and cuprous chloride solution is essentially the same, whether the solution contains carbonic oxide or not. Thus the E.M.F. of the combination  $\text{Pt} \mid \text{CuCl}_2 \mid \text{HCl} \mid \text{HgCl} \mid \text{Hg} \mid \text{HgCl} \mid \text{HCl} \mid \text{CuCl}, \text{HCl} \mid \text{Pt}$  is  $0.16$  volt; when the cuprous chloride solution is charged with carbonic oxide, the E.M.F. is  $0.135$  volt. As before, carbon may be substituted for platinum. When the platinum electrode immersed in the cupric chloride solution is replaced by copper, the E.M.F. is  $0.4$  volt. This arrangement leads up to Borchers' element,  $\text{Cu} \mid \text{CO} \mid \text{CuCl} \mid \text{O} \mid \text{C}$ , the basis of which is the combination  $\text{Cu} \mid \text{CuCl} \mid \text{C}$ , with an E.M.F. of  $0.45$  volt. When carbonic oxide is introduced at the copper electrode, and oxygen at the carbon electrode, the E.M.F. is not appreciably affected. The oxygen, however, prevents the separation of copper at the carbon electrode, and thus the element cannot assume the form  $\text{Cu} \mid \text{CO} \mid \text{CuCl} \mid \text{Cu}$ , the E.M.F. of which is practically nil. The carbonic oxide is oxidised to carbonic anhydride at the copper electrode, and the latter is undiminished. Thus Borchers' element is able to give a continuous current.

J. C. P.

**Connection between the Electrical Properties and the Chemical Composition of different kinds of Glass.** By ANDREW GRAY and JAMES J. DOBBIE (*Proc. Roy. Soc.*, 1898, 63, 38—44).—The authors, in conjunction with T. Gray (*Abstr.*, 1885, 470), previously established the general result that the electrical conductivity of lead glass increases with the amount of soda present, and decreases as the percentage of lead oxide rises.

In the present investigation, the specific resistance and specific inductive capacity of several glasses, made specially for the investigation, have been determined. The two lead glasses examined were almost free from soda, and had a higher percentage of lead oxide

(43 per cent. and 47 per cent.) than any previously used; they both had an extremely high specific resistance—too high to be measured. Another glass, described as barium aluminium borosilicate, had the very high specific resistance (ohms) of above  $59,000 \times 10^{10}$  at all temperatures up to  $140^\circ$ , thus behaving more like a lead glass than a lime glass. This glass shows scarcely any trace of dielectric polarisation. The effect that soda has in increasing the conductivity is shown in the case of a zinc soda 'Jena glass,' the specific resistance of which was  $596.5 \times 10^{10}$  at  $43^\circ$ , and  $0.200 \times 10^{10}$  at  $140^\circ$ .

The composition of each of the glasses examined is given in the paper. J. C. P.

**Galvanic Polarisation in Solutions of Alkali Sulphates.** By HANS JAHN (*Zeit. physikal. Chem.*, 1899, 29, 77—88).—The polarisation in  $N/8$  solutions of sodium, lithium, and ammonium sulphates was determined by the method previously employed by the author (Abstr., 1896, ii, 250; 1898, ii, 496). The values obtained are  $N/8$  sodium sulphate,  $E_0 = 2.55$  volts,  $E_{40^\circ} = 2.42$  volts;  $N/8$  lithium sulphate,  $E_0 = 2.65$  volts,  $E_{40^\circ} = 2.45$  volts;  $N/8$  ammonium sulphate,  $E_0 = 2.39$  volts,  $E_{40^\circ} = 2.23$  volts, the current varying from 0.0118 to 0.138 ampères. The author has previously shown that the polarisation is a function of the current, and the values obtained are found to be in good accord with those calculated by the use of his logarithmic formula  $E = a + b \log I$ , where  $I$  is the current strength. L. M. J.

**Electro-affinity: a New Principle of Chemical Classification.** By RICHARD ABEGG and GUIDO BODLÄNDER (*Zeit. anorg. Chem.*, 1899, 20, 453—499).—The theory of valency and constitutional formulæ, so useful in systematising organic compounds, fail when applied to inorganic compounds. The chief characteristic of the latter is their electrolytic dissociation, and this suggests that the attraction between an atom and electron would provide a more general basis of classification than the attraction between one atom and another. A measure of this electro-affinity (intensity of union between atom and electricity) is given by the E.M.F. necessary to destroy the union between atom and electron. The E.M.F. required to decompose a salt is an additive property of the anion and cation, and thus for each ion a number can be given which expresses the intensity of its union with electron. The cations, Na, Mg, Al, Zn, Cd, Pb, H, Cu'', Ag, Hg', are arranged in the order of their decreasing electro-affinity, and so similarly are the anions Cl, Br, I. It is then shown that various properties of inorganic compounds, such as solubility, degree of dissociation, and tendency to form complex or molecular salts, vary with the electro-affinity.

A salt will in general be soluble in proportion to the ease with which it splits up into ions. An example of this parallelism between electro-affinity and solubility is found in the increase of solubility in the halogen compounds of mercury, silver, or lead from iodide to chloride. Exceptions, however, are to be found, and the authors point out that the ion-solubility is not a simple function of the electro-affinity; another factor is the energy required to dissolve the union between atoms of the same compound, and this atom-affinity increases



enormously and rapidly in those cases where the electro-affinity is high. This explains probably why the alkali chlorides are less soluble than the iodides, and potassium salts in general less soluble than sodium salts.

The degree of dissociation of an electrolyte does not depend only on the electro-affinity of the component parts (sodium chloride and sodium iodide, for example, are dissociated to about the same extent); it depends also on the atom-affinity of the constituents and the solubility of the undissociated molecules. The electro-affinity and degree of dissociation may be more directly compared in the case of dibasic and tribasic acids, which are dissociated to a less extent than monobasic acids; the more numerous the charges an ion has to carry, the less will be the intensity with which they are held.

Parallelism is also traced between electro-affinity and the tendency to form complex compounds. In the latter, one of the ion-forming constituents is a molecular group, consisting of a 'single ion' (or ions), and an electrically neutral molecule ('neutral part'); thus in the anion  $\text{FeCy}_6$ , there are the single ions  $\text{Cy}_3$  and the 'neutral part'  $\text{FeCy}_3$ . For the stability of such molecular groups, salts with weak ions will be the most suitable 'neutral parts,' and it is found accordingly that the tendency to the formation of complex compounds increases as the electro-affinity decreases. The alkali metals are scarcely ever found in 'neutral parts,' whilst magnesium, aluminium, iron, copper, and silver are so in an increasing degree. The fact that in the electrolysis of complex compounds the 'single ion' alone is liberated, shows that the electro-affinity of the complex ion is greater than that of the 'single ion'; thus the weaker an ion is, the more will it tend to strengthen itself by the addition of a 'neutral part.' This is seen in the series  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{CN}$ , which show a gradually increasing tendency towards the formation of complex ions. Complex anions are more common than complex cations, because few anions have an electro-affinity comparable to that of the strong cations.

Another common 'neutral part' is ammonia, in the ammonia compounds of metallic salts; weak ions, such as copper and silver, have the greatest tendency to unite with ammonia. The addition of  $\text{NH}_3$  to the relatively weak ion  $\text{H}$  forms the strong ion  $\text{NH}_4$ . Hydrates also can in this manner be classified along with molecular compounds,  $\text{H}_2\text{O}$  being regarded as a 'neutral part.' The comparison of migration velocities supports the view that the ions are hydrated. There is probably a close connection between hydrated salt and hydrated ions, and it is noted that the salts with the weakest ions show the strongest tendency to have water of crystallisation.

Werner has shown that the hydrates and ammonia compounds may be regarded from one standpoint, and the authors have now extended this view to all molecular compounds.

J. C. P.

**Apparatus for Electrolysis.** By JOSEPH RIBAN (*Bull. Soc. Chim.*, 1899, [iii], 81—85).—In many electrolytic operations, it is important to know the current density, and this is usually determined from the formula  $ND_{100} = i/S$ , where  $i$  is the strength of current in ampères and  $S$  is the surface of the electrode in square decimetres.

In most cases, however, the current density is not the same over the whole surface of the electrode, and the above expression simply gives the mean value of this quantity; this is the case where conical and cylindrical electrodes are employed. In order to obtain a more uniform distribution of current density, the author advocates the use of hemispherical electrodes concentrically disposed, the outer electrode consisting of a platinum capsule, formed of a hemispherical portion, prolonged into a short cylindrical part, the inner electrode, which generally forms the anode, consisting of a platinum hemisphere surmounted by a cone. In this form of apparatus, the current intensity is constant for all sections of the electrode, except those at the surface of the liquid. The paper concludes with a description of clamps and supports suitable for electrolytic work. G. T. M.

**Magnetic Susceptibility of Liquid Oxygen.** By JOHN A. FLEMING and JAMES DEWAR (*Proc. Roy. Soc.*, 1898, 63, 311—329).—When a substance is introduced into a magnetic field of variable strength, a mechanical force is exerted on it, which depends on its magnetic susceptibility. If  $f$  be this force, then  $f = kVH.dH/dx$ , where  $V$  is the volume of the substance,  $H$  the field-strength, and  $dH/dx$  the rate of change of the field-strength;  $k$  is the difference between the magnetic susceptibility of the substance and that of the surrounding medium. By determining  $k$  for the same substance in two different media, the susceptibility of the one medium can be calculated from that of the other.

An electro-magnet was placed vertically, the soft steel core being fixed at a lower level than the bobbin; in the space thus left above the core and inside the coil, balls of silver, copper, bismuth, and glass were suspended from the one pan of a balance. The mechanical force exerted on the balls when the magnet was excited was measured by the change necessary in the counterpoise. The apparent susceptibility of each ball was determined first in air and then in liquid oxygen; in the latter case, a vacuum vessel filled with liquid oxygen occupied the space above the core.

The mean value of the susceptibility of liquid oxygen is found to be  $324 \times 10^{-6}$ . This holds for values of  $H$  between 500 and 2500 C.G.S. units; the susceptibility increases with low values of  $H$ . From the relation  $\mu = 1 + 4\pi k$ ,  $\mu$  (the magnetic permeability of liquid oxygen) is calculated to be 1.0041. The authors previously found, by a different method,  $\mu = 1.0027$ ; they consider the value 1.0041 much more probable.

The measurement of magnetic susceptibility at low temperatures is discussed and a method described of determining paramagnetic susceptibility. The susceptibility of manganous sulphate at  $25^\circ$  is to that at  $-180^\circ$  in the ratio of 1:3.32, that is, inversely as the absolute temperature. Other experiments with manganous sulphate indicate that paramagnetic susceptibility varies directly as the density. On the basis of these data, the susceptibility of liquid oxygen is calculated from that of gaseous oxygen, and found to be  $314 \times 10^{-6}$ , a value very close to that given by experiment. Hence the very large paramagnetic susceptibility of liquid oxygen is partly due to its low temperature.

J. C. P.

**Measurement of Low Temperatures.** By ALBERT LADENBURG and C. KRÜGEL (*Ber.*, 1899, 32, 1818—1822).—The author has employed Holborn and Wien's method (*Ann. Phys. Chem.* 1896, [ii], 59, 213) in which a thermo-element is used, but has standardised the galvanometer in a special manner, namely, by determining three instead of two fixed points by the aid of the hydrogen thermometer.

With the aid of this apparatus, the following data have been obtained.

Boiling points :—

Oxygen —  $181.4^{\circ}$ , nitrogen —  $142.4^{\circ}$ , methane —  $152.5^{\circ}$ , ethane —  $85.4^{\circ}$ , ethylene —  $102.65^{\circ}$ , propylene —  $50.2^{\circ}$ , trimethylene about —  $35^{\circ}$ , acetylene —  $83.8^{\circ}$ , toluene +  $110^{\circ}$ , ethylbenzene +  $135$ — $136^{\circ}$ , mesitylene +  $164^{\circ}$ , methylic formate +  $32$ — $33^{\circ}$ , ethylamine +  $19$ — $20^{\circ}$ .

Melting points :—

Nitrogen —  $150.0^{\circ}$ , ammonia —  $77.05^{\circ}$ , ethane —  $171.4^{\circ}$ , trimethylene —  $126^{\circ}$ , toluene —  $94.2^{\circ}$ , ethylbenzene —  $94.2^{\circ}$ , mesitylene about —  $59.6^{\circ}$ , cymene —  $75.1^{\circ}$ , methylic chloride —  $103.6^{\circ}$ , ethylic bromide —  $116.0^{\circ}$ , methylic alcohol —  $94.9^{\circ}$ , ethylic alcohol —  $112.3^{\circ}$ , ethylic ether —  $112.6^{\circ}$ , acetaldehyde —  $120.7^{\circ}$ , acetone —  $94.9^{\circ}$ , ethylene glycol —  $17.4^{\circ}$ , methylic formate —  $101.2^{\circ}$ , ethylic acetate —  $83.8^{\circ}$ , ethylamine —  $85.2^{\circ}$ .

J. J. S.

**Gradual Change of Glass and the Variation of the Zero Point of Thermometers.** By L. MARCHIS (*Zeit. physikal. Chem.*, 1899, 29, 1—26).—The variation of the zero point of a thermometer is an example of expansion hysteresis, and is a special case of the general case of gradual change studied by Duhem (*Abstr.*, 1897, ii, 439). If glass be heated from  $T_0$  to  $T_1$  the specific volume increases from  $V_0$  to  $V_1$ , but on again cooling to  $T_0$  the specific volume does not return to  $V_0$  but to a volume  $V_2$  which may be greater or less than  $V_0$ , and by repetition of the process the volume changes in the same manner but to a less extent until a final fixed value is reached. The variation of the zero point hence does not proceed with a definite velocity which is a function of the temperature to which it is heated (Young, *Nature*, 1890, 41, 152, 271, 288), as if kept at a constant temperature the variation is far less than when subjected to numerous temperature changes below this constant temperature, and the variation is not one for which a velocity can be calculated. The author describes the apparatus by which the thermometers could be subjected to definitely varying temperatures and the differences between new thermometers and those in use were investigated; many experiments were made but few of the experimental numbers are given in the present paper.

L. M. J.

**Heat, Energy, and Entropy.** By OTTO WIEDEBURG (*Zeit. physikal. Chem.*, 1899, 29, 27—50).—A theoretical paper, in which the thermodynamical deductions are obtained in a manner slightly different from the one usually adopted.

L. M. J.

**Heat of Dissolution.** By J. J. VAN LAAR (*Zeit. physikal. Chem.*, 1899, 29, 159—161).—A reply to Noyes (this vol., ii, 401), in which the author contends that the errors in Noyes' expressions are due to a confusion of the 'integral' with the 'actual' heat of dissolution

of a compound. In the thermodynamical methods originally employed by the author, this confusion cannot occur, and on this account those methods are preferable.

L. M. J.

**Cryoscopic Measurements.** By A. PONSOT (*Bull. Soc. Chim.*, 1899, [iii], 21, 356—361. Compare Abstr., 1897, ii, 88, 363, 440; 1898, ii, 555; this vol., ii, 357).—A further criticism of Raoult's conclusions, with remarks on the sources of error attending cryoscopic measurements.

N. L.

**Freezing Point of Mixtures of Acetic Acid and Water.** By LOUIS C. DE COPPET (*Ann. Chim. Phys.*, 1899, [vii], 16, 275—288).—The freezing points of mixtures of acetic acid and water cannot be represented by a single curve, but are found to lie on two intersecting curves which are each capable of prolongation beyond the point of intersection; the exact limit of the extension has not been determined. When solutions containing 56 to 64 per cent. of acetic acid are cooled, three types of crystals may separate, (1) ice, which floats on the surface of the liquid; (2) glacial acetic acid which accumulates at the bottom of the experimental tube; and (3) opaque, white crystals which have approximately the same density as the mother liquor; these consist of the cryohydrate, and are only formed spontaneously when the temperature is kept below  $-26.75^{\circ}$ . A solution containing 63.29 per cent. of acetic acid is placed in a freezing mixture until its temperature is  $-27.68^{\circ}$ , a fragment of ice is added, the temperature gradually falls to  $-28.87^{\circ}$ , and remains stationary for one minute, and during this interval ice separates; the temperature then rises rapidly to  $-25.42^{\circ}$  and glacial acetic acid is precipitated, it then falls to  $-26.75^{\circ}$ , and remains stationary for some time whilst the cryohydrate crystallises. However, it is not possible to bring about the separation of ice or glacial acetic acid from a solution containing 60.50 per cent. of acid; this mixture has only one freezing point,  $-26.75^{\circ}$ , and the constituents always crystallise together in the form of the cryohydrate. The composition of this product is not absolutely invariable, the percentage of acid varying from 59.8 to 61.0 per cent. The temperature  $-26.75^{\circ}$  is represented by the point of intersection of the two curves. One curve corresponds with the separation of ice from dilute acetic acid solutions and the other with the separation of the glacial acetic acid from its aqueous solutions.

G. T. M.

**Researches on the Polymerisation of Cyanogen Compounds.** By PAUL LEMOULT (*Ann. Chim. Phys.*, 1899, [vii], 16, 338—432).—The greater part of this work has already been published (compare Abstr., 1896, i, 70, ii, 11; 1897, i, 234, ii, 87; 1898, i, 117, 402, 458). The paper includes a discussion of the results obtained and additional thermochemical data.

	Molecular heat of combustion.	Molecular heat of formation.
Dicyanodiamide, $(\text{CN}_2\text{H}_2)_2$ ...	328.73 Cals.	-2.23 Cals.
Cyanuramide, $(\text{CN}_2\text{H}_2)_3$ ...	468.9	21.9
Cyanomethine, $(\text{CNMe})_3$ ...	845.8	30.50
Cyanoethine, $(\text{CNEt})_3$ ...	1311.7	54.5

When polymerisation is accompanied by a change of chemical functions, it will take place even if the reaction results in only a slight development of heat. The polymerisation of a mol. of cyanamide to dicyanodiamide is accompanied by evolution of 7 Cal., and the change to cyanuramide liberates 15 Cal. Similarly, when acetonitrile and propionitrile change into cyanomethine and cyanethine respectively, about 9 Cal. are evolved.

G. T. M.

**Thermal Relations of Normal Butylmalonic Acid.** By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1899, [iii], 21, 277—278).—The heat of solution of butylmalonic acid is  $-3.98$  Cal.

$C_7H_{12}O_4$  diss. + KOH, diss. =  $C_7H_{11}O_4K$  diss. develops  $+14.53$  Cal.

$C_7H_{11}O_4K$  diss. + KOH diss. =  $C_7H_{10}O_4K_2$  diss. „  $+13.47$  Cal.

$C_7H_{12}O_4$  diss. + 2KOH diss. =  $C_7H_{10}O_4K_2$  diss. „  $+28.00$  Cal.

The heat of solution of the anhydrous potassium salt is  $+5.00$  Cal. Calculated for the solid acid and potash, the heat of formation is given by :

$C_7H_{12}O_4$  sol. + 2KOH sol. =  $C_7H_{10}O_4K_2$  sol. +  $2H_2O$  sol. +  $46.80$  Cal.

The heat of formation of the normal potassium salt of normal butylmalonic acid has approximately the same value as those of its contiguous homologues, the numbers for isopropylmalonic, normal butylmalonic, and normal amylmalonic acids being respectively  $46.34$ ,  $46.80$ , and  $46.69$  Cal. In these three acids, the two carbonyl groups are at the same distance apart, and it is concluded that the molecular weight of the lateral hydrocarbon residue has a negligible influence on the acidimetric value of the molecule.

T. H. P.

**Compounds of Lithium, Sodium, and Potassium, with Mercury, as Indicated by the Specific Volumes.** By E. MAEY (*Zeit. physikal. Chem.*, 1899, 29, 119—138).—In a mixture, the specific volume is a linear function of the percentage content of one of the components, thus if  $V_1, V_2$  be the specific volumes of the components, and  $r$  the percentage of (2), then  $V = V_1 + (V_2 - V_1)r$ ; further, if in a mixture of two compounds the percentage of (2) is  $r$ , and in the two compounds themselves the percentages are  $r_1$ , and  $r_2$ , whilst  $q$  is the percentage of the second compound in the mixture, then  $r = r_1 + (r_2 - r_1)q$ . It follows therefore that the specific volume of the mixture is also a linear function of  $r$ . Hence, if in the case of a mixture of mercury with an alkali metal a curve is drawn for specific volume against percentage amount of alkali metal, it should consist of a number of straight lines, intersecting at points which indicate the composition of definite compounds. In this manner, the following compounds are found to exist:  $NaHg_5$ ,  $NaHg_2$ ,  $NaHg$ ,  $Na_3Hg$ ;  $LiHg_5$ ,  $LiHg_3$ ,  $LiHg$ ,  $Li_3Hg$ ;  $KHg_{11}$  or  $KHg_{12}$ ,  $KHg_3$ ,  $KHg_2$ ,  $KHg$ . Of these,  $NaHg$ ,  $KHg_2$ ,  $KHg$ , and the lithium compounds have not been hitherto observed. Many of the compounds were obtained crystalline, including a potassium compound,  $KHg_5$ , and the heats of formation of the sodium and potassium compounds were also determined.

L. M. J.

**Relation Between Osmotic Work and Osmotic Pressure.** By KONRAD DIETERICI (*Zeit. physikal. Chem.*, 1899, 29, 139—146).—A controversial paper, in which the author replies to the criticisms of

Noyes (this vol., ii, 357), and defends those views which the latter held to be erroneous. The deductions of Noyes are further considered to be inaccurate, and the corrections are given; they are, moreover, unjustifiable, being based on the assumption of a case which is incapable of experimental realisation. L. M. J.

**Determination of Molecular Weights from the Dissociation Pressures of Gaseous Hydrates.** By G. ROSSET (*Bull. Soc. Chim.*, 1899, [iii], 21, 361).—The pressure of dissociation of a gaseous hydrate, such as chloral hydrate, in contact with an aqueous solution is much greater, and capable of more accurate measurement, than the vapour pressure of the solution itself, and a definite relation exists between the two pressures, which may be expressed by the equation  $p^n p^{nl} = \text{constant}$ . It is therefore suggested that the comparison of the dissociation pressures of a suitable gaseous hydrate in contact with an aqueous solution and with pure water, would form a very sensitive method for determining the molecular weight of the dissolved substance. N. L.

**Gaseous Reactions in Chemical Kinetics. I.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 29, 147—159).—In spite of its importance and theoretical simplicity, the dynamics of gaseous reactions has been little studied. The form of the expression connecting the velocity of a reaction with the temperature is  $d. \log. k/dt = A/T^2 + B$ , where  $B$ , however, may be a function of  $T$ . It is doubtful whether the velocity becomes zero at the absolute zero of temperature in all cases, although this supposition is supported by the fact that in many gas reactions the temperature coefficients are approximately equal if the reactions become measurable at approximately equal temperatures. The author proposes to examine experimentally this question by the determination of the temperature variation of the decomposition of hydrogen iodide. Most cases of chemical equilibrium are due to the equal velocities of two reverse changes, but in some cases this is not so, and a reaction is under certain conditions brought to a standstill which may be regarded as a case of 'false equilibrium.' Examples of such a case are found in the formation and decomposition of hydrogen selenide (Pélabon, *Abstr.*, 1897, ii, 251) and in various oxidation phenomena, and the author considers these require further investigation. The results of the experimental work are deferred to later papers. L. M. J.

**Demonstration of the Law of Mass Action as Applied to Weak Electrolytes.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1808—1809).—It is well known that the addition of potassium or ammonium acetate to solutions of acetic acid diminishes the number of hydrogen ions present; this is usually demonstrated by the fact that acetic acid to which much potassium acetate has been added does not dissolve ferrous sulphide. It may also be shown by the fact that acetic acid containing a considerable amount of an acetate in solution is no longer capable of liberating nitrous acid from a nitrite. J. J. S.

**Velocity of Crystallisation. III.** By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1899, 20, 51—76. Compare *Abstr.*, 1898, ii, 425; this vol., ii, 272).—The author considers that the initial increase of

the velocity of crystallisation with undercooling, that is, the decrease of the velocity with rise of temperature, is due to the slow conduction of heat from the surface of crystallisation. The undercooling necessary for the maximum velocity should therefore be proportional to the latent heat of fusion per unit volume, and to the velocity itself, and inversely proportional to the conductivity. The effect of heat conduction is proved by enclosing a copper cylinder in an outer glass tube, leaving an annular space of 0.1 mm., in which the crystallisation-velocity is considerably increased in those limits within which it increases with undercooling, whilst it is also greater in narrow tubes than in broad tubes. If the constant maximum velocity of crystallisation is small, then, on account of the loss of heat, it may not be actually reached, and a maximum point is obtained (this vol., ii, 206). If a tube filled with undercooled benzophenone crystallising with its maximum velocity, is placed on a bath at 70°, the crystallisation is checked, but at about -40° the second modification of benzophenone forms, and on sowing the first modification in this, a cloudy mass results, containing also a third modification. If the temperature of the tube is now raised to -30°, the slight velocity of crystallisation of the first modification increases, and then very rapidly reaches its maximum value, but in narrower tubes, with hence better thermal conductivity, the temperature and velocity at which the sudden increase occurs is considerably raised, and numerous experiments are recorded to show this effect. The specific heat of the solid and liquid forms and the latent heat of fusion were determined for apiole, benzophenone, and betol, and the author hence calculates that for these compounds the temperature at which the velocity commences to decrease should, under adiabatic conditions, be: apiole, -40°; benzophenone, -15°; betol, +40°, the found values being respectively -2°, +8°, and +60°. These compounds, and probably all compounds, are polymorphous, and the conditions of crystallisation with the maximum velocity are determined for the three modifications of benzophenone, two modifications of apiole, three modifications of salol, and four modifications of betol. By sowing crystals of the third modifications (m. p. 25.2°) in a tube of undercooled benzophenone, a clear, crystalline mass is obtained, which by addition of the first modification changes into this compound, and owing to the cloudiness produced by the change the velocity can be measured. The curve is given for this transitive velocity, which increases to about 24°, remains constant to about 22°, and then decreases.

L. M. J.

**Diazotisation.** By ARTHUR HANTZSCH and M. SCHÜMANN (*Ber.*, 1899, 32, 1691—1703).—In order to study the velocity of the change represented by the equation  $R \cdot NCl : H_3 + HNO_3 = R \cdot NCl : N + 2H_2O$ , the nitrous acid is estimated from time to time by a colorimetric method. For this purpose, Kopp and Spiegel's diphenylamine test is unsuitable, owing to the heat which is developed on mixing the nitrous acid solution with the sulphuric acid in which the diphenylamine is dissolved; the best results are obtained by Trommsdorf's method, which depends on the development of a blue coloration in a solution of zinc iodide and starch, and can be used in *N*/100,000 solution.

The action is complete in about half an hour at  $0^{\circ}$  in  $N/100$  solution, but proceeds with suitable velocity at  $N/1000$ , whilst at  $N/100,000$  it only proceeds extremely slowly, especially in the last stages. The solutions used were therefore  $N/1000$ , and were diluted to  $N/100,000$ , in order to determine the nitrous acid. The blue coloration of the starch iodide takes some time to develop, and the comparison of tint is made from 15 to 60 minutes after adding the nitrous acid solution; for this reason, the values obtained in the initial stages of the reaction are too high, but in the later stages the error appears to be only slight.

The chief disturbing influence is caused by the formation of diazo-amido-compounds. In  $N/100$  solution, without any excess of acid, no separation takes place in the case of aniline, and at  $N/1000$ , although the solution becomes yellow after 24 hours, it still remains clear; parabrom- and paranitr-aniline, however, gave a large amount of the diazoamido-compound. The addition of 1 mol. of hydrochloric acid in excess produces a marked increase in the velocity, but no further change is produced by adding more acid. Thus aniline at  $N/1000$  and  $0^{\circ}$  had changed in half an hour to the extent of 52 per cent. without any excess of acid, but 65 per cent. had changed with 1 mol. of free hydrochloric acid; on the other hand, parabromaniline at  $N/1000$  and  $10^{\circ}$  had changed to the extent of 80 per cent. in half an hour, 95 per cent. in 3 hours, and 99 per cent. in 6 hours, when either 1 or 5 mols. of free hydrochloric acid were present.

In presence of an excess of acid, the velocity of change is the same for all bases; thus at  $N/1000$  and  $0^{\circ}$ , aniline, paratoluidine, metaxylidine, and parabromaniline had changed to the extent of 65 per cent. in half an hour, 82 per cent. in 2 hours, and 99 per cent. in 16 hours, the variation for the separate bases being only about 1 per cent., and easily accounted for by experimental errors. When no excess of acid was used, it was found that the strongest bases changed most rapidly towards the end of the action, but no marked difference occurred in the earlier stages; the weaker bases, however, soon gave irregular results, owing to the formation of diazoamido-compounds. The increase of velocity on the addition of an excess of acid is explained by the complete conversion of the base into the form of neutral salt or ion, owing to the disappearance of hydrolytic dissociation; the reaction is regarded as taking place between the ions,  $R \cdot \overset{+}{N} : H_3 + HNO_2 = R \cdot \overset{+}{N} : N + 2H_2O$ , and these are therefore the active agents in the change.

The temperature has a marked influence on the velocity; thus, parabromaniline in  $N/1000$  solution, with 1 mol. of free hydrochloric acid, had changed in half an hour to the extent of 64 per cent. at  $0^{\circ}$ , 80 per cent. at  $10^{\circ}$ , and 95 per cent. at  $20^{\circ}$ .

The reaction which takes place is of the second order, and the values obtained for the velocity-constant,  $C = x/(a-x)t$ , were 0.036 for aniline, 0.038 for toluidine, 0.041 for metaxylidine, and 0.045 for parabromaniline in  $N/1000$  solution with 1 mol. of free acid at  $0^{\circ}$ .

T. M. L.



**Aminolysis.** By HEINRICH GOLDSCHMIDT and RICHARD M. SALCHER (*Zeit. physikal. Chem.*, 1899, 29, 89—118).—The strength of bases is dependent on the degree of dissociation of the hydroxyl, but in the case of organic bases dissolved in certain solvents no hydroxyl group may be present. It has been shown (Abstr., 1896, ii, 515) that diazoamido-compounds are converted into amidoazo-compounds by aniline hydrochloride in aniline or other solution, and that the reaction is monomolecular, the velocity being proportional to the concentration of the aniline hydrochloride. Hence, if to a solution of the diazo-amido-compound in aniline a salt such as pyridine hydrochloride is added, the velocity is proportional to the concentration of the free acid, that is, to that of the aniline hydrochloride since the pyridine salt is undissociated, and the active mass of the aniline is constant. Hence, this concentration, which is that of the decomposed pyridine salt, may be found, and from this the equilibrium constants between the aniline and pyridine salts, or what the author terms the aminolytic constant. The velocity constants for the change from the diazo- to the amido-azo-compounds were determined for different acids, the values being—hydrochloric acid,  $-0.080$ ; hydrobromic acid,  $0.140$ ; nitric acid,  $0.116$ ; and orthonitrobenzoic acid,  $0.0088$ ; it is noticeable that the first three acids, although equally dissociated in aqueous solutions, have in this case different effects. The conversion velocity was next determined in the presence of pyridine and hydrochloric, hydrobromic, and orthonitrobenzoic acids; the aminolytic constants calculated as above were found to be  $2.36$ ,  $2.32$ , and  $2.23$ , so that the constant is independent of the acid employed. Various bases were then examined, and the following values for the aminolytic constant were obtained—quinoline,  $1.66$ ; pyridine,  $2.32$ ; tribenzylamine,  $2.95$ ; quinaldine,  $5.31$ ;  $\alpha$ -picoline,  $10.7$ ; *s*-collidine,  $287$ ; dimethylbenzylamine,  $10,500$ ; diethylbenzylamine,  $21,700$ ; triethylamine,  $434,000$ . The affinity constants of most of these bases have been found by Bredig, and those of the remainder were determined; it is seen that the aminolytic constants follow the same order as the affinity constants, and are approximately proportional to them, so that the base which in aqueous solution is the most highly dissociated can also remove the largest amount of acid from aniline hydrochloride in aniline solution. The exact import of this is not further discussed, but it is pointed out that it is possible that the strengths of acids may also be comparable under conditions which preclude dissociation.

L. M. J.

**Recognition of Racemic Compounds.** By ALBERT LADENBURG (*Ber.*, 1899, 32, 1822—1825. Compare Trans., 1899, 75, 466).—An exception to the generalisation previously made may occur when a diminution in the solubility of the racemic compound occurs, but is exactly counterbalanced by the amount of the dissolved optically active component. The question of racemism may then be solved by finding whether the solution is optically active or not; if it is active, then the original compound must have been racemic, if inactive, then the original was a mixture. This has been tested in several cases and found to hold good (compare Pope, Proc., 1899, 15, 73). J. J. S.

**Position of Helium, Argon, and Krypton in the Scheme of Elements.** By SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1898, 63, 408—411).—The elements are arranged in the order of their atomic weights on a line which traces out a figure-of-eight spiral. Each of the successive loops is divided into eight equal parts, and an element is placed at each point of division. Analogous elements are then found to be on the same vertical. The electropositive elements are on those parts of the curve which are leaving, the electronegative elements on those parts of the curve which are approaching, the middle line of the figure. The atomicity of the elements on the loops is given by the number of places they are removed from the middle line of the figure.

The elements occupying positions on the curve between the loops might be expected to be chemically and electrically neutral, and it is pointed out that helium, argon, and krypton (with atomic weights of 4, 40, and 80 respectively) would naturally occupy these positions, and that neon and metargon would also fall on the central neutral line of the figure. J. C. P.

**New Aspirator.** By ARTHUR ROSENHEIM (*Ber.*, 1899, 32, 1831—1833).—For use with a form of double aspirator similar to that devised by Fairley (*Thorpe's Dict. App. Chem.*, 1, 206), the author describes a simple automatic glass valve, which enables the four-way tap to be dispensed with, and obviates all fear of back pressure when the aspirating bottles are being interchanged.

J. J. S.

**Burettes and Separating Funnels.** By F. STÖBER (*J. pr. Chem.*, 1899, [ii], 59, 595—596).—When a burette with a tap or a pinchcock at the delivery end cannot be used, it is recommended to have a bent glass tube fitted with a pinchcock attached to the upper end of the burette. By opening the pinchcock, the liquid is delivered from the burette. This can be filled from the delivery end by use of a suction pump. When the burette is not in use, the delivery end is closed by a very small glass flask. A similar arrangement is suggested for separating funnels to allow of complete separation. R. H. P.

**Apparatus for Heating Sealed Tubes at a Constant Temperature.** By JOHN J. SUDBOROUGH (*J. Soc. Chem. Ind.*, 1899, 18, 16).—The apparatus has been devised for heating sealed tubes in the vapour of a liquid of high boiling point such as cumene or aniline. The tubes, which are kept in position by two copper discs, each perforated with four holes, are placed in a stout copper cylinder some 25 inches long and 6 inches in diameter, closed at one end and placed horizontally on an iron stand 9 inches high. The liquid is contained in a 150 c.c. dish, preferentially hammered out of the material of the cylinder itself, so as to avoid using rivets. On the upper side over the dish a copper tube is soldered, to which a Soxhlet's metal condenser is attached. A stout brass collar is soldered to the open end of the cylinder, which may be closed with a large brass cap screwing into the collar and fitted with a narrow strip of sheet cork.

L. DE K.

## Inorganic Chemistry.

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**High-Strength Hypochlorite Solutions.** By MAX MUSPRATT and E. SHRAPNEL-SMITH (*J. Soc. Chem. Ind.*, 1899, 18, 210. Compare this vol., ii, 281).—Solutions were prepared containing from 22–42 per cent. of available chlorine, and, after eliminating the iron, they were kept in closed earthenware bottles for seven weeks. The results, as tabulated, prove that from the point when salt begins to deposit to the point when it has practically all settled, the hypochlorite is not quite so stable as it was at lower strengths before any deposition of salt took place.

In the former experiments, a considerable amount of chlorate was formed, but owing to improved means of circulation and cooling, and to a better regulation of the amount of caustic soda, the formation of chlorate has been reduced by about 50 per cent. The authors have also succeeded in obtaining well-defined crystals of reasonably pure sodium hypochlorite. These form prisms of the quadratic system, are freely deposited from a solution containing 42 per cent. of available chlorine, and although still not pure, are much more stable than the solution from which they were formed.

L. DE K.

**Oxidising Action of Hydroxylamine.** By L. MARINO (*Zeit. anorg. Chem.*, 1899, 20, 452).—In reference to the work of Tanatar (this vol., ii, 285), it is pointed out that Piccini first described the action of hydroxylamine as an inorganic oxidising agent, and reserved for himself the complete investigation of the subject. This the author is now carrying out at Piccini's request.

J. C. P.

**Perborates.** By SIMEON M. TANATAR (*Zeit. physikal. Chem.*, 1899, 29, 162. Compare Abstr., 1898, ii, 427).—Perborates decompose gradually, for after keeping a year in corked vessels the ammonium salt was found to be considerably changed, the residue containing nitrite and nitrate; the sodium salt was also found, under similar conditions, to have lost 30 per cent. of active oxygen. This decomposition is more rapid in an atmosphere containing carbonic anhydride. The perborates are not formed by the action of chlorine on borates, and are decomposed by hypochlorites with the production of pure oxygen. A similar evolution of oxygen is brought about by the catalytic action of cobaltic oxide. They are also decomposed by the electric current, and do not appear to be formed by the action of ozonised oxygen on orthoborates.

L. M. J.

**Action of Ammonia and Amines on Silicon Chlorides.** By FELIX LENGFELD (*Amer. Chem. J.*, 1899, 21, 531–537).—On mixing benzene solutions of silicon tetrachloride and ammonia, the first product is *silicon tetramide*,  $\text{Si}(\text{NH}_2)_4$ , a white solid, which is extremely unstable, and even at ordinary temperatures loses ammonia and forms silicon di-imide,  $\text{Si}(\text{NH})_2$ . The product that is usually isolated has the empirical composition  $\text{SiCl}_4 \cdot 6\text{NH}_3$ , and yields one-third of its

ammonia when thrown into water; it is therefore regarded as a compound of silicon di-imide with ammonium chloride of the composition  $\text{Si}(\text{NH})_2, 4\text{NH}_4\text{Cl}$ . *Silicon tetrethylamide* is a colourless oil which boils at  $102^\circ$  under 20 mm. pressure; it keeps indefinitely in closed tubes, is decomposed by water, although not instantly, is soluble in most organic solvents, and dissolves in dilute nitric acid without complete decomposition.

T. M. L.

**Ammonium Hyposulphites.** By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1899, [iii], 21, 326—328).—When a solution of ammonium sulphite is agitated in the cold with metallic zinc, one-half of the salt is converted into the insoluble compound  $\text{ZnSO}_3, 2\text{NH}_3$  and the other half into normal ammonium hyposulphite. On filtering the liquid, the latter salt is obtained in solution free from zinc; the yield is 96—98 per cent. of the theoretical. The action of zinc on ammonium hydrogen sulphite (6 mols.), leads to the formation of ammonium hydrogen hyposulphite (2 mols.), normal ammonium hyposulphite (1 mol.), zinc sulphite (2 mols.), and the double salt  $\text{ZnSO}_3, 2\text{NH}_3$  (1 mol.).

N. L.

**Formation of Carbides of the Alkali and Alkaline-earth Metals and of Magnesium.** By HENRI MOISSAN (*Ann. Chim. Phys.*, 1899, [vii], 16, 145—152).—A *résumé* of work already published (*Abstr.*, 1898, ii, 332).

G. T. M.

**Cement from an Ancient Water Conduit.** By FRIEDRICH DÖRNER (*Monatsh.*, 1899, 20, 265—271).—A light grey cement of an irregular structure taken from the small water conduit of the theatre at Ephesus contained  $\text{CaO}$ , 52.65;  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , 0.27;  $\text{MgO}$ , 0.7;  $\text{Na}_2\text{O}$ , 0.5;  $\text{SiO}_2$ , 1.7,  $\text{CO}_2$ , 40.33, and  $\text{H}_2\text{O}$ , 0.98 per cent.; an ancient cement from Smyrna was found to have an almost identical composition. Both materials contained about 2.5 per cent. of organic matter, from which, by extracting with ether, evaporating, and recrystallising the residue from alcohol, a mixture melting at  $62.3^\circ$ , and containing about 10 parts of palmitic acid and 90 of stearic acid, was obtained. The residual dark brown liquid probably consisted of saturated and unsaturated fatty acids. The portion of the organic matter which is not extracted by ether is also insoluble in carbon bisulphide, benzene, or light petroleum, slightly soluble in water, and easily so in alkalis. From the alkaline solutions, acids precipitate dark-brown flakes. This substance seems to be a humin compound, although the amount of hydrogen (7.4 per cent.) is unusually high.

Cements made by mixing quicklime with linseed or olive oil crack, and set very slowly, but mixtures of slaked lime with these oils form good cements, the best results being obtained by using 2 parts of lime to 1 of olive oil. These ancient cements were probably made of a similar mixture, the proportion of organic matter having decreased during the long exposure, owing to decomposition and loss of all the glycerol.

E. W. W.

**Beryllium.** By PAUL LEBEAU (*Ann. Chim. Phys.*, 1899, [vii], 16, 457—503).—A detailed account of work previously published in an

abridged form (compare *Abstr.*, 1896, ii, 168, 169, 187; 1897, ii, 144; 1898, ii, 292, 511, 580, 581). G. T. M.

**Action of Water on Zinc and Galvanised Iron.** By HERBERT E. DAVIES (*J. Soc. Chem. Ind.*, 1899, 18, 102—105).—All kinds of water attack zinc or galvanised iron in the presence of air. Distilled or rain water has a decided solvent action, although after a time the greater part of the metal is reprecipitated. Hard waters dissolve a larger quantity, in which respect zinc differs from lead. When the metal gets gradually coated with hydrated zinc carbonate, the action is not altogether stopped, and the water may still contain 0·3 part of zinc per 100,000. It is not yet satisfactorily made out whether the continued use of water containing zinc is injurious to the system, but the metal may be detected in all the viscera. L. DE K.

**Reducibility of Metallic Oxides.** By HENRI HÉLIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 43—44).—The chemical properties of many metallic oxides undergo marked alteration when these substances are exposed to high temperatures. These changes may be due to polymerisation of the molecule of the oxide. Litharge when heated to 350° in a current of hydrogen loses some of its oxygen, but the reduction is never complete; the carbonate, however, on similar treatment, is completely reduced at 325°. The author supposes that litharge is a polymeride of PbO, and that the simple oxide is to be found only in normal salts such as the carbonate. G. T. M.

**Properties of Aluminium.** By ALFRED DITTE (*Ann. Chim. Phys.*, 1899, [vii], 16, 152—162).—The author's views on the alterable nature of this metal have been already quoted (compare this vol., ii, 225, 292, 425, 426). G. T. M.

**A Tungsto-potassic Tungstate.** By L. A. HALLOPEAU (*Bull. Soc. Chim.*, 1899, [iii], 21, 267—269).—After maintaining a mixture of tin and potassium paratungstate for an hour at a temperature sufficiently high to melt the tungstate, and treating the residue successively with boiling water, concentrated hydrochloric acid, a boiling 50 per cent. solution of potassium carbonate, and finally with hot water again, there remains a dark blue powder consisting of prismatic crystals of the composition  $K_2O, WO_3 + WO_2, 3WO_3$ . T. H. P.

**Double Chlorides and Bromides of Uranium.** By JULES ALOY (*Bull. Soc. Chim.*, 1899, [iii], 21, 264—266).—On passing the vapour of uranium tetrachloride, prepared by the action of chlorine on uranium carbide, over potassium or lithium chloride heated to dull redness, the latter gradually melts owing to its absorption of the uranium chloride, forming a double salt,  $UCl_4, 2KCl$  or  $UCl_4, 2LiCl$ ; these salts are pale green when first prepared, but are very hygroscopic, and rapidly darken as they absorb moisture from the air. They are very soluble in acetic acid, and dissolve also in water with development of heat, giving a strongly acid solution which oxidises slowly in the air at ordinary temperatures, and more rapidly when heated. The solutions are decomposed by water, so that when evaporated in a vacuum over sulphuric acid, crystals of alkali chloride are deposited, and a green,

uncrystallisable mass left behind. Alcohol gives a green solution which also rapidly oxidises and becomes yellow.

By similar methods, double chlorides of uranium and the alkaline earth metals can be prepared; in this case, care must be taken to dry the chloride before heating, which must not be carried too far. The compounds formed, which have the composition  $UCl_4.MCl_2$  (where M corresponds with Ca, Sr, or Ba), are of a deeper green colour than those yielded by the alkali metals; like the latter, they are decomposed by water and cannot be obtained crystalline by evaporating their solutions in a vacuum.

The above method may be employed to prepare double bromides corresponding with the chlorides already described. The double bromides are of a deeper green colour than the chlorides, to which they are analogous in properties.

The double chlorides of uranyl and the alkali metals may be obtained by passing dry chlorine over gently heated uranous oxide, by which means uranyl chloride is formed; the latter is then led over the alkali chloride with which it combines, forming golden-yellow, fusible compounds.

T. H. P.

**Compounds of Titanium Dioxide with Sulphuric Acid.** By BLONDEL (*Bull. Soc. Chim.*, 1899, [iii], 21, 262—264).—By heating a concentrated sulphuric acid solution of titanium dioxide in a sealed tube at  $120^\circ$ , a mass of silky crystals is obtained which are soluble in water acidified with hydrochloric acid, and have the composition  $2TiO_2.3SO_3 + 3H_2O$ . On raising the temperature to  $225^\circ$ , the mass changes into rhomboidal crystals of the composition  $TiO_2.SO_3$ , which are slowly decomposed by water into a basic sulphate and sulphuric acid; by maintaining the solution at  $225^\circ$ , the whole of the titanium present can be separated in this form. Rutile readily dissolves in concentrated sulphuric acid when heated to about  $200^\circ$ , but if the temperature of the acid exceeds  $225^\circ$ , a layer of sulphate forms on the mineral, and protects it from further action.

On diluting a solution of titanium dioxide in concentrated sulphuric acid with an equal volume of water, the liquid at any temperature above  $100^\circ$  deposits long needles which have the composition  $TiO_2.SO_3 + 2H_2O$ , and are readily soluble in water. If 1 part of the dioxide be dissolved in 2 parts of concentrated sulphuric acid, and water be added to the extent of  $1\frac{1}{2}$  times the weight of the solution, the liquid deposits sulphates, the composition of which varies with the temperature of deposition; those formed at  $100^\circ$  correspond with the formula  $2TiO_2.SO_3 + Aq$ , and those at  $130^\circ$  to  $7TiO_2.2SO_3 + Aq$ . Solutions of titanium dioxide in concentrated sulphuric acid, when diluted with from 2 to 10 times their weight of water and heated, deposit various sulphates at temperatures below  $175^\circ$ , but above this temperature the anhydrous dioxide crystallises out; if, however, the solutions be strongly diluted (with 100 to 1000 parts of water) at ordinary temperatures, the compound  $5TiO_2.SO_3 + 5H_2O$  is obtained, whilst at  $100^\circ$  the deposit consists of the dioxide with traces of sulphuric acid which cannot be removed by washing.

When a sulphuric acid solution of the dioxide diluted with slightly

ammoniacal water is allowed to evaporate in a vacuum, cubic crystals of the composition  $2\text{TiO}_2 \cdot 2\text{SO}_3 \cdot \text{NH}_4\text{O} + 3\text{H}_2\text{O}$  separate; these crystals, which present tetrahedral hemihedrism, are slowly decomposed by water and effloresce in the air.

T. H. P.

**New Soluble Antimonic Acid and its Salts.** By JEAN B. SENDERENS (*Bull. Soc. Chim.*, 1899, [iii], 21, 47—58).—When antimony trichloride is treated with concentrated nitric acid, a vigorous action occurs, and a clear liquid is obtained, which on dilution yields a white deposit; this substance is washed with cold water and exposed to the air for 3 months at ordinary temperatures; its composition then corresponds with the formula  $\text{Sb}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ . The orthohydrate,  $\text{Sb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , analogous to orthophosphoric acid, is obtained on drying the hexahydrate over concentrated sulphuric acid for 3 weeks; when heated to  $200^\circ$ , it passes into the hydrate  $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , corresponding with pyrophosphoric acid; at  $300^\circ$ , the metahydrate,  $\text{Sb}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , is produced; at  $400^\circ$ , the anhydrous oxide,  $\text{Sb}_2\text{O}_5$ , is obtained, which, when heated to redness, yields the tetroxide.

The recently precipitated hexahydrate is soluble in water to the extent of 22 grams of  $\text{Sb}_2\text{O}_5$  per litre, but a solution of this strength gradually becomes turbid, and a precipitate appears, which increases until the amount of dissolved oxide falls to 3 grams per litre. The precipitate, when dried, has a composition corresponding with  $\text{Sb}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , and is probably identical with the hydrate described by Fremy, by Daubrawa, and by Beilstein and Blaese (Abstr., 1889, 1123). The author's experiments show that this hydrate is less readily dehydrated on heating than was stated by these observers, and his results agree with the more recent work of Baubigny (Abstr., 1897, [ii], 351).

A solution of the soluble acid containing 8 grams of  $\text{Sb}_2\text{O}_5$  per litre is comparatively stable; when titrated with caustic potash solution in the presence of phenolphthalein, the quantity of alkali required for neutralisation corresponds with the formation of the salt  $\text{KHSb}_2\text{O}_6$ , whereas with baryta the salt  $\text{BaSb}_2\text{O}_6$  is indicated. The antimonates derived from the soluble acid are obtained by adding metallic acetates to its solutions; they bear a certain resemblance to the salts prepared by Ebell (Abstr., 1890, 126).

The *nickel, cobalt, copper, cadmium, and mercuric* salts, when dried in air, have the general formula  $\text{R}'\text{Sb}_2\text{O}_6 + 5\text{H}_2\text{O}$ , and when placed over concentrated sulphuric acid they lose  $3\text{H}_2\text{O}$ , and have a composition corresponding with  $\text{R}'\text{Sb}_2\text{O}_6 + 2\text{H}_2\text{O}$ . The *calcium, manganese, and zinc* salts have the general formula  $\text{R}''\text{Sb}_2\text{O}_6 + 6\text{H}_2\text{O}$ , and when dried over sulphuric acid they correspond with  $\text{R}''\text{Sb}_2\text{O}_6 + 2\text{H}_2\text{O}$ . The *lead* salt, when dried in air, contains  $9\text{H}_2\text{O}$ , and sulphuric acid removes  $7\text{H}_2\text{O}$ , leaving  $\text{PbSb}_2\text{O}_6 + 2\text{H}_2\text{O}$ . The *ammonium* and *potassium* salts, when dried in air, contain  $5\text{H}_2\text{O}$  and  $7\text{H}_2\text{O}$  respectively; in the presence of sulphuric acid, they form salts of the type  $\text{R}_2\text{Sb}_2\text{O}_6 + 2\text{H}_2\text{O}$ . All these salts, when heated to  $300^\circ$ , lose the remaining water.

G. T. M.

**Antimony Pentasulphide. II.** By OTTO KLENKER (*J. pr. Chem.*, 1899, [ii], 59, 353—433. Compare this vol., ii, 490, and Bosek, *Trans.*, 1895, 520).—It is shown that antimony pentasulphide, on

account of the ease with which it undergoes decomposition, is not a suitable compound on which to base quantitative estimations of antimony.

The precipitate obtained on passing a stream of hydrogen sulphide into a moderately strong alkaline solution of a quinquevalent compound of antimony consists of a mixture of antimony trisulphide and sulphur (pure antimony trisulphide remaining on extraction with carbon bisulphide). Neutral or acid solutions give a precipitate composed of a mixture of the two sulphides and free sulphur, the largest proportion of pentasulphide being formed from a solution containing 12 per cent. of free hydrochloric acid. As the quantity of free acid further increases, the proportion of pentasulphide formed decreases until from a solution containing 27 per cent. of free hydrochloric acid, antimony is not precipitated. On acidifying a solution of Schlippe's salt, the precipitate obtained consists of a mixture of trisulphide and sulphur, with varying proportions of pentasulphide.

The precipitate obtained from a warm (about  $75^{\circ}$ ) acid solution has the composition  $\text{Sb}_2\text{S}_3 + 2\text{S}$ . On the other hand, antimony pentasulphide is not affected by treatment with organic solvents boiling below  $100^{\circ}$ .  
R. H. P.

**Colloidal Metals: Colloidal Bismuth and Copper.** By ALFRED LOTTERMOSER (*J. pr. Chem.*, 1899, [ii], 59, 489—493. Compare Vanino and Treubert, this vol., ii, 428).—When bismuth nitrate (2 mols.) is dissolved in water containing a little nitric acid, and a solution of ammonium citrate is added until the resulting precipitate dissolves, the solution made alkaline with ammonia, added to a solution of stannous chloride (3 mols.) prepared in a similar manner, and the mixture quickly heated, colloidal bismuth is deposited in the form of a very fine, black precipitate. This will dissolve in water, but is reprecipitated on addition of a solution of any salt, or of an acid. It is transformed into the insoluble form of the metal by continued boiling of its solution, or by a large excess of stannous salts.

Similarly, if alkaline solutions of cupric and stannous chlorides are warmed with a solution of sodium citrate, a precipitate is obtained consisting of a mixture of colloidal copper and colloidal stannic acid.  
R. H. P.

**Ruthenium and its Compounds.** By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1899, 29, ii, 312—318).—By fusing ruthenium with potassium hydroxide and gradually adding small quantities of nitre until the ruthenium is all dissolved, a green mass is formed, which changes to an orange colour on cooling; on repeatedly treating this mass with concentrated hydrochloric acid, a product is obtained containing more and more potassium ruthenochloride, which has, however, not been obtained in the pure state.

By dissolving barium ruthenate in fuming hydrochloric acid, and repeatedly evaporating to dryness with the acid, a residue is obtained which dissolves in water; after removing the barium by adding an excess of sulphuric acid and evaporating the solution, a dense, pale red liquid is obtained, probably containing ruthenium sulphate, which could not, however, be obtained crystalline.



When hydrogen sulphide acts in the cold on Joly's potassium chloronitrosoruthenate (Abstr., 1889, 352), partial precipitation of a ruthenium sulphide occurs, and the liquid assumes an intense azure tint. When separated from the precipitate, this liquid is quickly decolorised, even in the dark, and deposits a sulphur compound of ruthenium; if, however, the hydrogen sulphide is removed by passing a rapid current of carbonic anhydride through the liquid, the latter remains unchanged for a long time. By acting on a solution of the potassium chloronitrosoruthenate with sulphurous anhydride, the liquid changes from red to dark green, and finally to violet, and on evaporation deposits a blue powder, which may be purified by precipitating its aqueous solution with alcohol, and separated from alkali chloride by washing with dilute alcohol. This powder behaves like a colloidal substance, and has not been obtained crystalline; it is stable at about  $220^{\circ}$ , but above that temperature loses sulphurous anhydride and becomes black. T. H. P.

**Composition of Osmiamates.** By L. BRIZARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 170—172).—The author confirms the compositions for these compounds previously arrived at by Joly (Abstr., 1891, 1433), namely,  $\text{KO}_2\text{OsNO}_3$ ,  $\text{NH}_4\text{OsNO}_3$ , and  $\text{AgOsNO}_3$ . The osmium was estimated by precipitation as sulphide, and subsequent reduction to the metal. J. J. S.

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## Mineralogical Chemistry.

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**Artificial Production of Diamond in Silicates.** By I. FRIEDLÄNDER (*Geol. Mag.*, 1898, 5, 226, and *Jahrb.f. Min.*, 1899, 1, Ref. 202, from *Verh. d. Ver. z. Beförd. d. Gewerbeleisses, Berlin*, Feb., 1898).—A small piece of olivine was fused in the gas-blowpipe, and the molten mass stirred with a rod of graphite; after cooling, the silicate was found to contain vast numbers of microscopic (0.001 mm.), brown crystals, but only in the parts which had been in contact with the carbon. These crystals were identified as diamond, since they are octahedral or tetrahedral in form, are unattacked by hydrofluoric and sulphuric acids, have a high refractive index, sink slowly in methylenic iodide, burn away when heated in oxygen, and are unaltered if heated in a current of carbonic anhydride; the stony matter containing them scratches corundum. This suggests that the diamonds of South Africa may have been formed by the action of a molten silicate on graphite or carbonaceous shales, such as those which are penetrated by the olivine-bearing rock of Kimberley. L. J. S.

**Laboratory Production of Asphalts from Animal and Vegetable Materials.** By WILLIAM C. DAY (*Amer. Chem. J.*, 1899, 21, 478—499).—By distilling together fat pine wood and fresh herrings from the Delaware river, from an iron retort, and passing the vapours through a red-hot iron tube, there was produced water and an oil of sp. gr. 0.9837 containing 84.28 per cent. of carbon and 10 per cent. of

hydrogen. After distilling the oil up to a temperature of about  $425^{\circ}$ , a residue was left in the retort, which solidified to a black, shining mass, showing conchoidal fracture, brittle, and pulverising to a brownish-coloured powder slightly darker than the powder of the natural asphalt 'gilsonite' from Utah, which it closely resembled. The analysis of the two materials gave the following figures:

	C.	H.	N.	S.	O.	Ash.
Artificial .....	86.56	7.06	1.91	0.08	4.39	—
Natural .....	85.83	10.59	2.59	0.26	0.63	0.10

The solubilities were as follows:

	Natural.	Artificial.
Carbon bisulphide .....	99.50	(1) 100.00 per cent.
		(2) 81.44 "
Turpentine .....	97.34	49.48 "
Ether .....	73.08	67.03 "
Light petroleum.....	63.08	46.70 "
Alcohol .....	34.81	48.40 "

Both substances are similarly acted on by nitric acid, which completely dissolves the material, with copious evolution of brown fumes, and the production of a dark red solution which, when diluted with water, yields a flocculent precipitate much resembling freshly precipitated ferric hydroxide. Both substances yield solid, volatile bases when extracted with dilute sulphuric acid.

On distilling fish alone, an emulsion was obtained which was separated by warming into water and a yellow oil. On boiling down the oil in an iron crucible, a black, elastic solid was produced, which could be easily cut but not pulverised, although, when struck with a hammer, it would break with a conchoidal fracture.

The analysis (C = 76.51 and 77.36; H = 9.08 and 9.12; N = 4.19 and 4.27; S = 0.19) is somewhat similar to that of the natural asphalt elaterite from Utah (C = 73.11 and 73.88; H = 9.46 and 9.45), which it somewhat resembles. The percentage solubilities were carbon bisulphide, 68.19; turpentine, 47.36; ether, 59.17; light petroleum, 35.19; absolute alcohol, 51.07. Much ammonia was produced during the distillation, and basic nitrogen compounds could be extracted from the solid by means of dilute sulphuric acid.

The distillation of pine wood gave water and an oil of sp. gr. 0.992. After distilling off more than half the oil, the residue solidified to a black, shining mass, very brittle, and showing a conchoidal fracture; the sp. gr. was 1.0825. The analysis (C = 86.20; H = 8.28; N = 0.29; O = 5.23; S, trace) resembles that of Utah nigrite (C = 83.33; H = 8.69; S = 0.42; Ash = 0.12). The percentage solubilities were, carbon bisulphide, 99.26; turpentine, 96.29; ether, 96.13; light petroleum, 90.12; absolute alcohol, 61.60. The material did not yield any basic substances when extracted with sulphuric acid.

When wood and fish are distilled together, the amount of oil produced is less, and the amount of water is greater, than when they are distilled separately; this is due to the fact that the oxygenated compounds from the fish are largely reduced by the hydrocarbons from the

wood during the passage through the red-hot tube, thus affording a method of preparing an asphalt containing a moderate percentage of nitrogen, but a low percentage of oxygen.

The paper contains a discussion as to the origin of natural asphalts and bitumens. T. M. L.

**Bismuthiferous Molybdenite.** By LÉOPOLD MICHEL (*Bull. Soc. franç. Min.*, 1899, 22, 29—30).—Large, steel-grey, crystalline plates with a bright metallic lustre gave, on analysis,

Mo.	Bi.	Fe.	S.	Total.
40.10	28.37	trace	30.74	99.21

At first sight, the mineral is apparently homogeneous, but when the cleavage plates are examined under a lens they are seen to enclose much bismuthite, so that the material is really an intimate mixture of molybdenite and bismuthite. L. J. S.

**Colouring Substances contained in Amethyst, Citrine and Burnt Amethyst.** By ARNOLD NABL (*Monatsh.*, 1899, 20, 272—281).—When amethyst is strongly heated, its colour changes to yellow and the absorption spectrum of the calcined stone, like that of citrine, closely resembles the spectrum of ferric oxide or of a ferric compound. The absorption spectrum of amethyst is almost identical with that of a solution of ferric thiocyanate in ether, and the colouring matter of amethyst, moreover, resembles this compound in becoming yellow when heated at 180° and regaining its original colour after a time when cold. Two specimens of amethyst were found to contain respectively 0.52 and 0.53 per cent. of sulphur, although the amount of carbon, according to Heintz (*Ann. Phys. Chem.*, 60, 519), is 0.0027 per cent., which would only correspond with 0.0072 of sulphur on the thiocyanate hypothesis. The manner of occurrence of amethyst and of citrine is also in accordance with the presence of ferric thiocyanate in the former and its change into the latter by heat, for citrine is generally found in crystalline fragments and but rarely in crystals; these crystals have, however, the same properties and form as amethyst. E. W. W.

**Corundum from the Appalachians.** By J. VOLNEY LEWIS (*Trans. Amer. Inst. Mining Eng.*, 1896, 25, 852—906).—A general account is given of the occurrence of corundum in the Appalachian crystalline belt. In the descriptions of the rocks, the following mineral analyses are given:

I.—Enstatite from the enstatite-rock at Corundum Hill, Macon Co., N. Carolina. The partial alteration of the enstatite to talc accounts for the presence of water. Analysis I by C. Baskerville.

II.—Bright, grass-green hornblende, sp. gr. 3.075, which with some anorthite forms amphibolite at Buck Creek, Clay Co., N. Carolina. Under the microscope, it is seen to enclose grains of chrome-spinel. On account of the grass-green colour, this hornblende has often been

called smaragdite, but it contains much more alumina than the original smaragdite.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	MnO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	51·64	0·12	—	9·28	31·93	0·56	0·45	—	—	5·45	99·43
II.	44·38	17·32	0·38	3·83	15·48	0·90	11·51	1·24	0·38	4·63	100·05

L. J. S.

**Artificial Cassiterite.** By J. H. L. VOGT (*Zeit. Kryst. Min.*, 1899, 31, 279—280. Compare Abstr., 1896, ii, 307).—The crevices in the hearth of a furnace used for the oxidation of metallic tin to pulverulent tin oxide were found to contain crystals of cassiterite, both simple and twinned, and up to 1 cm. long. Since salt, fluor spar, &c., were not present, the crystals have been formed by the direct oxidation of the tin without the presence of so-called "agents minéralisateurs." The usual occurrence of minerals containing boron and fluorine with tin-stone suggests that, in most cases, the natural mineral has been formed by sublimation, as in the synthetical methods of Daubrée and others.

L. J. S.

**Monazite from Finland.** By WILHELM RAMSAY and A. ZILLIACUS (*Zeit. Kryst. Min.*, 1899, 31, 317—318; from *Öfvers. Finska Vet.-Soc., Förhandl.*, 1897, 39).—The pegmatite veins in the parishes of Sordavala and Impilaks on the northern shore of Lake Ladoga, contain monazite and other minerals rich in rare earths. A crystallographic description is given of the monazite. The indices of refraction for yellow light are,  $\alpha = 1.7863$ ,  $\beta = 1.7879$ ,  $\gamma = 1.8372$ ;  $2V = 12^\circ 30'$ ; the optic axial plane is perpendicular to  $b(010)$  and  $Bx_a \wedge c'$  about  $= +4^\circ$ . Analysis I is of fresh, transparent, yellow monazite, sp. gr. 5.163; II is of reddish-brown, decomposed monazite, sp. gr. = 4.88.

	P <sub>2</sub> O <sub>5</sub> .	SiO <sub>2</sub> .	SnO <sub>2</sub> .	ThO <sub>2</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	(Di, La) <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	Loss on ignition.	Total.
I.	26·81	1·22	0·84	5·65	31·63	29·68	2·86	0·68	0·39	0·40	100·16
II.	21·50	3·62	—	9·50	53·31		3·22	—	—	2·76	—

L. J. S.

**New Minerals from Chili.** By ANDREAS ARZRUNI, KONSTANTIN THADDÉEFF, and A. DANNENBERG (*Zeit. Kryst. Min.*, 1899, 31, 229—247).—These notes on various minerals, by the late A. Arzruni, are completed and edited by A. Dannenberg, who gives the new name arzrunite; the chemical portion is by K. Thaddéeff.

**Arzrunite.**—This forms a drusy, crystalline crust, of a bright blue-green colour, in the cavities of a quartzose veinstone from Mina Buena Esperanza, Challacollo, prov. Tarapaca, Chili. The small crystals are hexagonal prisms with a prism angle of  $60^\circ$ , but the optical characters show them to be orthorhombic;  $a:b:c = 0.5773:1:0.4163$ . Analyses I and II are on material from different specimens; the second was more greenish than blue. After deducting quartz, limonite, gypsum, and epsomite (lanarkite,  $\text{PbSO}_4 \cdot \text{PbO}$ , was also present), the formula is given as  $\text{PbSO}_4 \cdot \text{PbO} + 3(\text{CuCl}_2 \cdot \text{H}_2\text{O}) + \text{Cu}(\text{OH})_2$ . Associated with the arzrunite are small, colourless crystals, with the angles of daviesite.

*Stelznerite*.—This new mineral occurs at Remolinos, Vallinar, Chili, as fine, green, transparent, prismatic crystals, resembling brochantite in appearance. The system is orthorhombic;  $[a:b:c = 0.50368:1:0.70585]$ . The optic axial plane is  $c(001)$ . Sp. gr. 3.884. Analyses III and IV (IV by Schröcker) agree with the formula  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ . No water is lost at  $160-170^\circ$ .

*Rafaelite*.—Translucent, violet-red needles, with zonal bands of colour, form a crystalline crust on galena, quartz, and celestite, with schwartzembergite and arzrunite, from Mina San Rafael, Sierra Gorda, Chili. Goniometrical and optical measurements are given, and qualitative tests showed it to be an oxychloride of lead. [This is identical with paralaurionite (this vol., ii, 433. See *Nature*, 1899, 60, 238)].

*Utahite*.—This mineral, previously only known as minute scales from Utah, is now described from Mina Santa Rosa, Guanaco, Taltal, Chili, as small, thick, rhombohedral crystals;  $cr = 52^\circ 49'$ . The crystals are dark yellowish-brown, with zonal bands of colour; they exhibit anomalous biaxial optic figures. Anal. V gives the formula  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ , whilst Damour's analysis of the material from Utah gave  $3\text{FeO}_3 \cdot 3\text{SO}_3 \cdot 4\text{H}_2\text{O}$ , and showed the presence of some arsenic.

*Brochantite*.—Analysis VI, of material from Mina Monte Cristo, Paposa, Chili, agrees with the usual formula,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ .

	$\text{SO}_3$	Cl.	PbO.	CuO.	$\text{Fe}_2\text{O}_3$	CaO.	ZnO.	$\text{H}_2\text{O}$	Insol.	Total.
I.	8.07	14.39	31.41	21.39	0.70	1.70	n.d.	—	13.60	—
II.	13.06	9.46	33.38	14.54	1.81	1.87	4.08	11.01	8.88	98.09
III.	22.40	—	—	67.08	0.34	0.06	—	10.22	0.44	100.54
IV.	22.19	—	—	64.01	1.14	0.57	—	10.70	1.42	100.03
V.	26.83	—	—	—	58.51	—	—	[12.47]	2.19	100.00
VI.	17.37	—	—	68.82	2.07	0.05	—	11.51	0.23	100.05

A new *Bismuth basic Carbonate*.—This forms a pale yellow botryoidal coating of small, spherical, crystalline aggregates on quartz, from Schneeberg, Saxony. Microscopical examination seems to show that the mineral is tetragonal. Analysis gave:

$\text{Bi}_2\text{O}_3$	CaO.	$\text{Fe}_2\text{O}_3$	$\text{CO}_2$	$\text{H}_2\text{O}$	Insol.	Total.
81.90	3.20	1.50	4.10	0.90	8.33	99.93

After deducting quartz, calcite, and limonite, this gives the formula  $5\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot \text{CO}_2$ . The variations in composition of massive, earthy bismuthite may be perhaps explained by the mixing of  $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot \text{CO}_2$  and  $\text{Bi}_2\text{O}_3$ .  
L. J. S.

*Hydrated Sodium Silico-aluminate*. By CHARLES FRIEDEL (*Bull. Soc. franç. Min.*, 1899, 22, 17—18).—A new analysis of the hydrated sodium silico-aluminate, prepared by Georges Friedel (*Abstr.*, 1896, ii, 482) by the action of caustic soda solution on muscovite at a high temperature, gave:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Total.
38.98	32.95	19.09	3.19	5.80	100.01

This gives the simpler formula,  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot \text{H}_2\text{O}$ . It approaches to thomsonite in composition.  
L. J. S.

**Sodium Silico-aluminate.** By GEORGES FRIEDEL (*Bull. Soc. franç. Min.*, 1899, 22, 20—25).—The substance described was produced together with nepheline and the orthorhombic hydrated sodium silico-aluminate (see preceding abstract) by the action of 9 per cent. soda solution on muscovite at a temperature of 508—510°; it was only once produced, and other attempts failed. The colourless, regular octahedra are shown by the optical examination to be pseudo-cubic, and to be built up of 24 monoclinic individuals. Analyses correspond with the formula  $8\text{SiO}_2, 3\text{Al}_2\text{O}_3, 6\text{Na}_2\text{O}$ . Sp. gr. 2·660. L. J. S.

[**Mineral Analyses.**] By L. G. EAKINS (*Zeit. Kryst. Min.*, 1899, 31, 287—288; from 17th Ann. Rept. U.S. Geol. Survey, 1896, pt. II, 278, 451, 454).—The following analyses of Colorado minerals are given in geological papers by Whitman Cross (pp. 269—403) and S. F. Emmons (pp. 411—472).

I. A complicated intergrowth of augite and hornblende in gneiss from the Silver Cliff district. Cross considers the intergrowth to be original and not paramorphic.

II. Psilomelane on rhyolite from Silver Cliff: it contained also  $\text{ZnO}$ , 2·80;  $\text{Sb}_2\text{O}_3$ , 0·12, and traces of Co, Sr, Li.

III. Kaolinite derived from the rhyolite at Silver Cliff; it contained also  $\text{CaO}$ ,  $\text{MgO}$ , and alkalis.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{MnO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$	Total
I.	48·72	9·27	3·77	6·34	0·34	—	16·79	14·67	—	0·19	0·18	100·27
II.	2·30	1·81	0·34	—	5·71	76·18	0·83	0·29	3·46	0·81	5·35	100·00
III.	68·16	17·68	—	—	—	—	—	—	—	—	12·76	98·60

L. J. S.

[**Cummingtinite from Brazil.**] By EUGEN HUSSAK (*Zeit. prakt. Geol.*, 1898, 353).—In a paper (pp. 345—357) on the rocks and minerals of the gold-bearing quartz and pyrites deposits of Passagem in Minas Geraes, the following description is given of cummingtinite. With granular quartz and some pyrrhotite and a green spinel, it forms a cummingtinite-schist which carries some gold. It is straw-yellow to light brown and asbestiform, and resembles anthophyllite in appearance; sp. gr. 3·2; angle of optical extinction on the plane of symmetry, 12°. Analysis gave,

$\text{SiO}_2$	$\text{Fe}_2\text{O}_3 + \text{MnO}$	$\text{MgO}$	$\text{CaO}, \text{Al}_2\text{O}_3, \text{Alkalis}, \text{Loss on ignition}$	Total
[53·81]	36·29	9·90	traces	100·00

L. J. S.

[**Mineral Analyses.**] By WILLIAM F. HILLEBRAND (*Zeit. Kryst. Min.*, 1899, 31, 286; from 16th Ann. Rept. U.S. Geol. Survey, 1895, Pt. II, 123, 127).—The following analyses of minerals are given in a paper (pp. 1—209) by Whitman Cross and R. A. F. Penrose on the geology and mining industries of the Cripple Creek district, Colorado.

Soft, light-green chloropal from the Ida May mine gave the results under I. Red jasper in the ore-veins of the Victor mine gave II; it contained also traces of  $\text{BaO}$ ,  $\text{MgO}$ ,  $\text{Li}_2\text{O}$ .

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	P <sub>2</sub> O <sub>5</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	41.80	—	—	trace	37.20	1.10	—	—	19.90	100.00
II.	72.46	2.52			17.88	0.14	1.08	0.06	5.70	99.84

L. J. S.

**Rocks and Laterite from the Seychelles.** By MAX BAUER (*Jahrb. f. Min.*, 1898, ii, 163—219).—The Seychelles are one of the few groups of small oceanic islands consisting mainly of plutonic rocks. Granite and some syenite are penetrated by dykes of felspar-porphry, hornblende-vogesite, diorite, and diabase; and sedimentary rocks are represented by baked shales at the granite contacts. A detailed petrographical description is given of these rocks.

Opal sinter derived from the syenite gave analysis I; it is optically isotropic. Anal. II is of an adinole or hornfels in contact with the granite. Analyses I—IV, by C. Busz.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	88.65	1.04	1.50	—	trace	—	—	8.36	99.55
II.	75.76	13.95	—	1.23	trace	4.15	5.36	0.50	100.95
III.	52.06	29.46	4.64	—	trace	—	—	14.40	100.59
IV.	3.88	49.89	20.11	—	—	—	—	25.98	99.86

Laterite is of wide distribution and is several metres thick; it has been formed *in situ* from the various rocks, and granite-laterite (anal. III), and diorite-laterite (anal. IV) are distinguished. It is reddish-brown, incoherent, and sandy. Thin sections under the microscope show the structure of the original rock; the quartz grains are unaltered, whilst the felspar, hornblende, and mica are altered to a colourless, scaly aggregate of minute birefringent plates; iron hydroxides fill cavities and are present as colouring matter. Analyses III and IV were made on material dried at 115°. The aluminium and iron hydroxides are dissolved out by boiling hydrochloric acid, leaving a residue of sandy quartz. The material is, therefore, not a silicate as formerly supposed. Deducting the silica as quartz and the iron as limonite, the aluminium hydroxide corresponds approximately with hydrargillite (Al<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O), with perhaps some admixed diaspore (Al<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O), this representing the fine, scaly material pseudomorphous after the felspar, &c.

Laterite and bauxite are compared; they are practically the same in chemical composition and microscopical characters, and are the result of the leaching out of silica and alkalis with the retention of the structure of the original rock. It is suggested that bauxite has been formed in the hotter climates of the Tertiary epoch. L. J. S.

**Dykes containing Huronite.** By ALFRED E. BARLOW (*Zeit. Kryst. Min.*, 1899, 31, 293; from *Ottawa Naturalist*, 1895, 9, 25—47).—An examination of dyke-rocks from various parts of Canada, shows that huronite is of fairly wide distribution. Thin sections show that the mineral is a basic plagioclase more or less altered to saussurite. Analysis by B. J. Harrington of the least altered of the phenocrysts



of plagioclase, sp. gr. 2·679, in diabase from the Nipissing district, Ontario, gave,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Loss on ignition.	Total.
54·19	28·42	0·77	0·41	trace	10·47	0·52	4·47	0·63	0·59	100·47

L. J. S.

**Oligoclase from Victoria.** By ALFRED W. HOWITT (*Rept. Australian Assoc. Adv. Sci.*, 1898, 7, 375—377).—Rounded crystals of felspar collected from volcanic detritus at Mount Anakies, in Victoria, gave the following results on analysis by F. E. A. Stone, and the corresponding angles of optical extinction are *c*(001) and *b*(010). The material is therefore oligoclase, Ab<sub>5</sub>An.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> (+ Fe <sub>2</sub> O <sub>3</sub> ).	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.	Extinction on <i>c</i> .	<i>b</i> .
I.	62·98	21·88	2·78	trace	5·00	1·90	94·54	+ 3° 7'	+ 12° 30'
II.	62·22	22·42	3·34	trace	6·14	2·30	96·42	+ 3 3	+ 12 19

L. J. S.

**Meteorite from Meuselbach, Thuringia.** By GOTTLÖB E. LINCK (*Ann. k.k. naturhist. Hofmus., Wien*, 1898, 13, 103—114).—This stone was seen to fall at Meuselbach, near Amt-Gehren, on May 19th, 1897; it weighs 870 grams; sp. gr. 3·47. It is light grey in colour, and finely granular, with white and greenish grains and chondrules. Nickel-iron, troilite and chromite are of irregular distribution. The 7·89 per cent. of nickel-iron has the following composition, agreeing with kamacite, (NiCo)Fe<sub>8</sub>.

Fe.	Ni.	Co.	Cu.	Total.
85·04	13·61	1·35	trace	100·0

The portion (53·62 per cent.) of the stony matter soluble in aqua regia gave analysis I, corresponding with olivine, (Fe<sub>2</sub>Mg<sub>2</sub>)<sub>2</sub>SiO<sub>4</sub>, and the insoluble portion (38·49 per cent.) gave the results under II corresponding with bronzite, (FeMg<sub>4</sub>)SiO<sub>3</sub>. A bulk analysis made on another portion of the meteorite gave III; also nickel-iron 7·78.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	FeS.	Chromite.	Total.
I.	32·07	0·24	22·27	30·06	0·52	0·32	trace	14·52	—	100·00
II.	52·33	7·21	11·01	21·87	3·75	3·45	trace	—	0·88	100·50
III.	40·23	2·85	15·82	24·98	2·44	1·58	trace	5·76	0·35	101·79

Under the microscope, the following (in order of predominance) were seen: Olivine, bronzite, nickel-iron, troilite, colourless glass, chromite, brownish glass, and an undetermined cubic mineral. The order of formation is: Chromite, olivine and bronzite, nickel-iron, troilite, cubic mineral, colourless glass. The structure of the stone is hypidiomorphic-granular, and suggests that the minerals are primary, and that they have solidified from fusion, rather than that they are of secondary clastic origin.

L. J. S.

**Composition of the Water from Wells on the Sea Coast.** By P. GUICHARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 79—81).—Analyses of well water have shown that there is very little relationship between this water and that of neighbouring rivers. The water level of the

wells in the neighbourhood of the estuary of the Somme rises and falls with that of the sea, although the small amount of chloride present in the well water shows that there is no direct communication between the wells and the sea.

G. T. M.

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## Physiological Chemistry.

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**Diastatic Action of Pancreatic Juice.**—By BENJAMIN K. RACHFORD (*Amer. J. Physiol.*, 1899, 2, 483—495).—A very small quantity of hydrochloric acid has little or no retarding influence on the diastatic action of pancreatic juice, although larger quantities materially retard it. Acid proteids increase the activity. Sodium carbonate is very destructive; bile slightly helps the action and neutralises the retarding influence of hydrochloric acid and of sodium carbonate. Bile itself has some diastatic power.

W. D. H.

**The First Product of the Gastric Digestion of Casein.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, 27, 297—302). Under favourable circumstances, casein is wholly digested by gastric juice; under unfavourable circumstances (too low a temperature, or too little digestive fluid), there is a residue of paranuclein. Before this, however, there is a primary stage in which the casein is converted into a proteose which contains all the phosphorus of the original proteid. Casein and caseinogen are in this respect alike.

W. D. H.

**Formation of Scatoleacetic Acid during the Putrefaction of Proteid.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, 27, 302—305).—Scatoleacetic acid is not exclusively a product of the activity of anærobic organisms, but is found in other cases associated with scatolecarboxylic acid.

W. D. H.

**Coagulation of Proteid by Electricity.** By W. B. HARDY (*J. Physiol.*, 1899, 24, 288—304).—Under the influence of a constant current, the particles of proteid in a boiled solution of egg-white move with the negative stream if the reaction of the fluid is alkaline, with the positive stream if the reaction is acid. The particles under the directive action of the current aggregate to form a coagulum. The action of the current is explained on the lines of Quincke's theory of electric endosmose.

W. D. H.

**Heat Rigor in Cold-blooded Animals.** By HORACE M. VERNON (*J. Physiol.*, 1899, 24, 239—287).—The results obtained are mainly confirmatory of those of Brodie and Richardson, who showed that the successive shortenings that a muscle undergoes when it is gradually heated occur at the coagulation temperatures of the various proteids in muscle described by Halliburton, and later by von Fürth.

W. D. H.

**Quantitative Relations of Protagon to the Medulla of Nerves.** By ALFRED NOLL (*Zeit. physiol. Chem.*, 1899, 27, 370—398).—Analyses of protagon from ox-brain give numbers which do not differ markedly from those of previous workers. The amount of protagon in the normal white matter of the brain (ox, dog, cow, man) varies from 19·4 to 21·8 per cent. of dry substance; in the white matter of the cord, from 22 to 25 per cent.; in nerves, from 7 to 12 per cent.; in grey matter, from 1·2 to 4·8 per cent. After Wallerian degeneration in nerves, the amount of protagon diminishes. This confirms what has been previously shown to occur by Mott, Barratt, and Halliburton in degenerative processes in the central nervous system. W. D. H.

**A Comparison of the Ash of the Young Animal and that of the Milk.** By EMIL ABDERHALDEN (*Zeit. physiol. Chem.*, 1899, 27, 356—367, 408—462).—The result of the analysis of the ash of newborn guinea-pigs, and of their milk, bears out what Bunge has already shown to be the case in other animals, namely, the close correspondence between the two.

The second paper is a continuation of a previous research (this vol., ii, 232), it being now extended to include other animals. Analytical details are throughout given in full. W. D. H.

**Estimation of Urinary Indican.** By JACOB BOUMA (*Zeit. physiol. Chem.*, 1899, 27, 348—355).—By Wang's method (this vol., ii, 458), the amount of indican in normal urine is found to be 5 milligrams a day; in pathological urines, this may rise to 18 milligrams.

By Obermayer's method (*ibid.*), the amount comes out 20 per cent. less. This is shown to be due to the fact that washing with 45 per cent. alcohol partly dissolves the indigo. W. D. H.

**Hæmatoporphyrinuria.** By EBERHARD NEBELTHAU (*Zeit. physiol. Chem.*, 1899, 27, 324—334).—A case of hæmatoporphyrinuria is described. The pigment is precipitated by acetic acid, and 1130 c.c. of urine were found to contain 0·04 gram of it; the urine also contained excess of urobilin. W. D. H.

**Chemistry of Malignant Tumours.** By EUGEN PETRY (*Zeit. physiol. Chem.*, 1899, 27, 398—407).—Extracts of cancerous tumours were made with 0·6 per cent. solution of sodium chloride, then with cold water, and finally with dilute alkali. From these extracts, the total proteid was estimated; albumin, globulin, and nucleo-proteid were found. There is increase of nucleo-proteid as compared with normal tissues. In a sarcoma, there was very little nucleo-proteid. There is, in these tumours, a considerable amount of proteid which is not coagulable by heat. By auto-digestion at the room temperature, this albumose-like proteid increases in quantity. W. D. H.

**Analysis of the Pulmonary Ossifications of "Entèque."** By CH. PORCHER (*Bull. Soc. Chim.*, 1899, [iii], 21, 248—250).—Animals which have succumbed to the disease known as "entèque" in the Argentine Republic have a characteristic ossification of their pulmonary tissue. This ossified material consists of a number of dense,

hard spines, the composition of which is practically the same as that of ordinary compact bone. J. J. S.

**Inflammation Caused by the Vapours of Nitrogen Chloride.** By W. HENTSCHEL (*Ber.*, 1899, 32, 1878).—The author states that violent inflammation of the mucous membrane of the throat is caused by inhaling the fumes of solutions of nitrogen trichloride; although, at first, apparently not harmful, these give rise after some months to very pronounced ill effects. W. A. D.

**Physiological Action of Extracts of Sympathetic Ganglia.** By ALLEN CLEGHORN (*Amer. J. Physiol.*, 1899, 2, 471—482).—From considerations as to the similarity of structure between sympathetic ganglia and suprarenal medulla, the effect of injecting glycerol and aqueous extracts of the ganglia into the circulation of animals was investigated. These extracts produce a fall of blood pressure which can be counteracted by suprarenal extract. The lowering of blood pressure is produced by the action of the extract on the neuro-muscular mechanism of the blood vessels; the tonus of the heart muscle is lowered, the latent period and relaxation period of skeletal muscle are lengthened; there is no action on the pupil. Extracts of brain, cord, spinal ganglia, and nerves produce no fall of blood pressure. W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Laboratory Sterilising Apparatus.** By JEAN HAUSSE (Bull. Soc. Chim., 1899, [iii], 21, 250—253).—The apparatus consists of a porcelain funnel with a perforated plate, and fitted into the mouth of a kind of separating funnel, which, in its turn, fits into the mouth of a flask connected with a filter pump; all parts of the apparatus are heated to 125°; boiling water and kieselgühr are run on to a double layer of filter paper placed on the plate of the funnel, and in this way a layer of moist kieselgühr, 0·5—1 mm. thick, is deposited, which may be employed for sterilising purposes. According to the author, a layer of the kieselgühr, which does not allow the passage of air under a pressure of 1 kilo., acts as a perfect steriliser to any liquid filtered through it, whilst it permits the passage of 15—20 times as much liquid as does an equal surface of porous porcelain. J. J. S.

**Schizomycetic Fermentation.** By OSKAR EMMERLING (Ber., 1899, 32, 1915—1918).—From a solution of malic acid, in which fermentation had been induced by inoculation with one drop of the liquid from putrefying flesh, a pure culture has been obtained of the *Bacillus lactis aërogenes*, first discovered by Escherich in the intestines of sucklings; it is a short, thick, non-mobile bacillus, and was identified by the form of its colonies, the milky-white appearance of the gelatin culture, the absence of spores, and especially the absence of colour in Gram's test. In a solution of bouillon and sugar, it develops hydrogen

and carbonic anhydride in molecular proportion. The pure culture acts on malic acid, reducing it to succinic acid almost quantitatively according to the equation  $3C_4H_6O_5 = 2C_4H_6O_4 + C_2H_4O_2 + 2CO_2 + H_2O$ . Alcohol is not produced, but traces of formic acid can be detected. The conversion of malic acid into succinic acid by brewers' yeast is due to bacteria, and does not take place with pure cultures. König has shown that tartaric acid is largely reduced to succinic acid by *Bacterium termo*, but *Bacillus aërogenes* appears to cause decomposition in other directions.

T. M. L.

**Ionisation and Toxic Action of Metallic Salts: Copper Sulphate and *Penicillium Glaucum*.** By LOUIS MAILLARD (*Bull. Soc. Chim.*, 1899, [iii], 21, 26—29).—The toxic action of copper sulphate solutions on *Penicillium glaucum* decreases when the ionisation of the salt is diminished by the addition of another sulphate. This fungus was grown in nutritive solutions containing varying amounts of copper and ammonium sulphates; on comparing the solutions containing the same amount of the ammonium salt, the development of the organism is found to become slower as the quantity of copper sulphate increases, whereas the inhibitive action of equal quantities of the latter salt decreases as the dose of ammonium sulphate increases.

G. T. M.

**Distribution and Functions of Cane Sugar in Plants.** By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1899, 27, 267—291. Compare Abstr., 1895, ii, 364).—Cane sugar is widely distributed in the ripe seeds of plants, although often it is present only in small amount. It is also present in the seeds of conifers. It is doubtless of importance as a reserve material, to be used as soon as germination begins; but as it increases as growth goes on, it must fulfil other uses as well. Accompanying the cane sugar, other soluble sugars capable of inversion are also present, sometimes in larger quantities.

W. D. H.

**Rôle of Iron Compounds and of Humic Substances in the Coloration of Water. Separation of these Substances under the Influence of Sunlight.** By W. SPRING (*Bied. Centr.*, 1899, 28, 429; from *Bull. Acad. roy. Belg.*, 1897, 34, 578—600).—Sea, lake, and river water might be expected to have a brown colour, when the amounts of iron and organic matter they contain are considered, similar to the colour produced by mixing dilute solutions of ferric chloride and peat-water. Such solutions, however, when exposed to light, gradually lose their dark colour, the change being accompanied by a separation of solid matter. It is concluded that the ferric salt oxidises the organic matter, and that the product has the property of forming insoluble compounds with metallic oxides. The function of iron in purifying natural waters is thus comparable with that of hæmoglobin in blood.

N. H. J. M.

**Curdling of Milk after Addition of Soluble Calcium Salts.** By PAUL VIETH (*Bied. Centr.*, 1899, 28, 418—419; from *Milchzeit.*, 1897, 193).—Hillmann found that the presence of soluble calcium

salts gave rise to increased production of cheese, but in practice the increase was less than in experiments on a small scale.

In the experiments now described, which extended over several months, calcium chloride in quantities of 5, 7·5, and 10 grams was added to 100 kilograms of milk. Increased production of cheese was only observed in one case, and the increase was very small (0·3 per cent.); whilst in other cases there was a slight decrease in the amount of cheese. It is, however, pointed out that in no case was the quality of the cheese injured, and it is thought possible that addition of calcium salts may sometimes be of importance, for instance, after milk has been pasteurised.

N. H. J. M.

**Changes in the Surface and Subsoil of Peat-land under the Influence of Cultivation and of Manure.** By G. SCHLIEBS and H. MINSEN (*Bied. Centr.*, 1899, 28, 361—365; from *Mitt. Arbeiten. Moorversuchs-Stat., Bremen*, 4. Ber.; *Landw. Jahrb.*, 1898, 27, *Ergänz.-Bd.*, IV, 525—547).—The more or less humified soil of peat-land as affected by tillage and manure is generally much less than 25 cm. deep, the subsoil being strongly acid peat which is usually not penetrated by the roots of crops. Manure constituents which reach the subsoil are therefore lost, and the loss is greatest in the case of newly cultivated peat-land which has only a slight power of absorption.

The effect of manuring on the surface soil was to increase the potash and phosphoric acid, but there was no increase in nitrogen when sodium nitrate had been applied, even in cases in which the nitrate could not have been completely used up. Generally, the increase of manure constituents in the soil is the greater the less complete the manuring with other constituents. Peaty soil which has been normally manured for some time accumulates so much potash and especially phosphoric acid that the amounts of manures may without injury be reduced; in such cases, it suffices to apply a slight excess over the amount removed by the crop. This conclusion is in accordance with the observation that the drainage from peat land contains but little potash.

Manuring with potash salts gives rise to loss of lime; basic slag may then be applied.

Loss of manures in the subsoil is greater in arable land than in meadows, and the loss is sufficiently great to render the adoption of subsoil-liming a very important question.

N. H. J. M.

**Peat Litter: Investigation of Soil Samples from Manure Heaps.** By ADOLF EMMERLING (*Bied. Centr.*, 1899, 28, 365—367; from *Landw. Wochenbl., Schleswig-Holstein*, 48, No. 2).—Kainite, gypsum, and peat-meal all diminished or hindered loss of ammonia; but with gypsum, which was the more effective, as much as 50—60 per cent. of the total ammonia was lost in a week. Peat-meal retained ammonia during the first few days better than afterwards; its use is recommended for the absorption of liquid manure, but it should be renewed every day.

Peaty soil and subsoil, on which manure had been kept, was sampled to the depth of 10, 40, and 50 cm. and analysed. It was found that the percentage of nitrogen was high, whilst the percentages



of phosphoric acid, and especially of potash, were very high. In the case of potash, the amount was even greater in the subsoil than at the surface, indicating that the power of absorption was exhausted in the surface soil. The amount of ammonia was also greatest in the subsoil.

N. H. J. M.

**Ammonium Salts and Chili Saltpetre [as Manures].** By PAUL WAGNER (*Bied. Centr.*, 1899, 28, 367—370; from *Deut. landw. Presse*, 1898, Nos. 30—31. Compare *Abstr.*, 1898, ii, 258).—With regard to statements recently made that the production of ammonium salts would have increased long ago if agriculturists had required it, it is pointed out that the 2,000,000 cwt. produced in Germany have been entirely consumed there, and that considerable amounts of ammonium salts have been imported in addition.

The conditions which affect the action of ammonium salts and nitrates are of various kinds. The former have the advantage that, until nitrified, the nitrogen is fixed in the soil. In the case of sodium nitrate, the soda is often of use in light soils in increasing the power of retaining water, in supplying nitrogen and phosphoric acid to the plants, and also, to some extent, in compensating for a deficiency of potash. On the other hand, with clay soils, sodium nitrate gives rise to the production of hard crusts, rendering the application of lime necessary.

The author advises caution in accepting the one-sided results of those interested in ammonia production, and criticises the experiments of Klöpfer (*Deut. landw. Presse*, 1898, Nos. 25—26; and this vol., ii, 512).

N. H. J. M.

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## Analytical Chemistry.

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**Employment of Adsorption in Analytical Separations.** By FRIEDRICH GOPPELSROEDER *Zeit. anal. Chem.*, 1899, 38, 291—292).—With reference to Trey's paper (this vol., ii, 182), the author directs attention to the fact that at various dates, commencing with 1861, he has published papers dealing very extensively with this subject (*Verhand. Naturforsch. Ges. Basel; Mitt. Sect. Chem. Gewerbe des k. k. Technolog. Gewerbe-museums in Wien*, 1888—1889). Amongst other applications of the method, he has employed it for the separation of mixed dyes. M. J. S.

**Indicators for Alkalimetry:** By F. GLASER (*Zeit. anal. Chem.*, 1899, 38, 273—278).—The Association of Bavarian Industrial Chemists at Speyer (see *Zeit. Untersuch. Nahr. Genussmittel*, 1899, 61) adopted a division of indicators into three groups, of which the following is an extension:

Group 1 (sensitive to alkalis).—(a) Tropæolin OO. (b) Methyl-ethyl-orange, dimethylamidoazobenzene. (c) Congo-red, benzopurpurin, iodeosin, cochineal. (d) Lacmoid.

Group 2.—(a) Fluorescein. (b) Alizarin, archil, hæmatoxylin,

gallein. (c) Litmus. (d) *p*-Nitrophenol, tincture of guaiacum. (e) Rosolic acid.

Group 3 (sensitive to acids).—(a) Tropæolin OOO. (b) Phenolphthalein, turmeric, curcumin W, flavescin (Abstr., 1881, 193). (c)  $\alpha$ -Naphtholbenzeïn. (d) Poirrier's blue C<sub>4</sub>B.

In each group, the earlier members are more sensitive to alkalis and less so to acids than the later members. Those in group 2 are intermediate in sensitiveness between the other groups. By titrating the same acid with indicators of different groups, information may be obtained as to the relative strength of its acidity. Thus, if one acid can be titrated with equal sharpness by either litmus or lacmoid, whilst another can be titrated sharply with litmus but not with lacmoid, the former is the stronger acid of the two. In this way, it may be shown that in a homologous series of organic acids containing the same number of carboxyl groups, decrease in strength of acidity is concurrent with increase in molecular weight, and that among acids of equal basicity and approximately equal molecular weight, the strength of acidity increases with increase in the number of hydroxyl groups.

For the titration of bases, all the indicators can be used only when strong fixed bases are in question, the general rule being that an indicator shows a sharp colour change only when the product of the reaction is neutral to that indicator. Even to indicators which are not highly sensitive to acids, the mineral acid salts of weak bases react acid, probably in consequence of dissociation by water, in which condition the stronger component exhibits its action on the indicator. The ammonium salts of mineral acids react acid with all indicators, although only feebly with those of group 1. This is not the case with the normal salts of the fixed bases with mineral acids, but at high dilutions it is necessary to have regard to the hydrolysis of the indicator itself, and attention is directed to the use made of an ethereal solution of iodeosin by Mylius and Förster (Abstr., 1891, 1136). A similar dissociation occurs when a salt of a weak acid and strong base is dissolved in water, and therefore such salts react alkaline to indicators of the first and second groups. Water itself exhibits an acid reaction with the members of the third group, but an alkaline reaction with those of group 1, so that at very high dilutions a sensible excess of the respective reagents must be added to arrive at the point of apparent neutrality. It follows that in all cases where a weak acid in dilute solution is titrated by an alkali, using an indicator of group 3 (as in wine analysis, and the estimation of the Reichert-Meissl value of butter), the results may be seriously too high unless the alkali has been standardised under the same conditions of indicator and dilution. When working with 150–200 c.c., a sufficiently accurate correction may be made by deducting 0.3 c.c. of *N*/10 alkali in the case of wine or beer, and 0.2 c.c. in that of the Reichert number from the amount required to give a permanent red colour with phenolphthalein. The presence of carbonic anhydride, or partial carbonatation of the alkali has not the injurious influence formerly attributed to it.

The effect of acid phosphates has in some cases been overlooked.

Thus, the latest draught of an agreement for establishing uniform methods of analysing foods throughout the German Empire leaves optional the use of litmus or phenolphthalein for the titration of the acid in beer. In consequence of the presence of acid phosphates, phenolphthalein in some cases indicates more than twice as much acid as does litmus. M. J. S.

**Estimation of Iodine by Sodium Thiosulphate in the Presence of Cyanides.** By W. CARRICK ANDERSON and ANDREW SMITH (*J. Soc. Chem. Ind.*, 1899, 18, 118—119).—Sulman and Teed have stated (*ibid.* 1898, 17, 963) that cyanogen bromide may be accurately titrated by adding excess of potassium iodide and acidifying with hydrochloric acid; 1 mol. of cyanogen bromide liberating 2 mols. of iodine, besides yielding 1 mol. of hydrogen bromide and 1 mol. of hydrogen cyanide; if the liquid contains excess of cyanides, there will, of course, be a large excess of the latter, but this is stated not to interfere with the usual titration of the iodine with sodium thiosulphate.

It now appears from the tabulated experiments conducted by the authors that, although mere traces of hydrogen cyanide do not interfere, relative large proportions render the process quite useless. This is due to the formation of cyanogen iodide. L. DE K.

**Estimation of Oxygen in Gaseous Mixtures by Titration.** By GRIGORI V. CHLOPIN (*Chem. Centr.*, 1899, i, 372; from *J. Russ. phys.-chem. Ges.*, 30, 750—760).—A 150 c.c. flask is provided with a doubly perforated india-rubber cork. Through one of the openings passes a glass tube reaching nearly to the bottom of the flask, whilst the other holds a short glass tube. Each is fitted with an india-rubber tube which may be closed at a marked spot by means of a pinchcock. The true content of the flask is found by filling it with water up to the pinchcocks and weighing. By means of bellows or of an aspirator, the flask is filled with the air to be tested, and is placed in a water-bath having the temperature of the gaseous mixture. After temperature and pressure have been recorded, the flask is closed by means of the pinchcocks. Through the smaller tube is now introduced first 15 c.c. of a solution made by dissolving 40 grams of crystallised manganous chloride in 100 c.c. of water, and then 15 c.c. of a solution prepared by dissolving 30 grams of potassium iodide and 32 grams of sodium hydroxide in 100 c.c. of water. The apparatus is closed and frequently shaken for 4—5 hours. The end of the reaction is known by the blackish precipitate assuming a yellowish-brown colour. Finally, 25 c.c. of strong hydrochloric acid is added and the liberated iodine is titrated with *N*/10 sodium thiosulphate, using starch water as indicator.

1 c.c. of thiosulphate represents 0.5592 c.c. of oxygen.

L. DE K.

**Estimation of Sulphur in Roumanian Petroleum.** By G. FILITI (*Bull. Soc. Chim.*, 1899, [iii], 21, 338—341).—The estimation of the sulphur in petroleum by the ordinary methods of oxidation is unsatisfactory and attended by various sources of error. Excellent

results are obtained by combustion with oxygen in the calorimetric bomb in presence of a little water. Employing this method, six specimens of petroleum from Câmpina were found to contain 0.202—0.245 per cent. of sulphur, whilst six specimens of Bustenari petroleum yielded 0.118—0.193 per cent.

MARCELLIN BERTHELOT (*ibid.*, 513) points out that, in conjunction with André and Matignon, he had already established the use of the calorimetric bomb for the analysis of sulphur compounds. N. L.

**Preparation of Standard Solutions of Sulphuric Acid.** By ARTHUR MARSHALL (*J. Soc. Chem. Ind.*, 1899, 18, 4—6).—The standardising of sulphuric acid by processes depending on the accurate weighing of substances supposed to be of known composition, is objected to, and it is held that Pickering's accurate determinations of the densities of sulphuric acid solutions (*Trans.* 1890, 59, 64—184) provides a means of preparing standard solutions with far greater accuracy. Sulphuric acid of great purity is diluted with half its volume of water, and when cold its sp. gr. is taken at 18°, or 15.5°, or 15° by means of a 25 c.c. Sprengel tube. This acid keeps for any length of time, and from it standard solutions of any required strength may be rapidly prepared. To save calculation, the author appends two tables, one for specific gravities at 15° and the other at 18°. L. DE K.

**Technical Method for the Direct Estimation of Nitrogen in Illuminating and other Gases without the Aid of "Gas, Analysis Apparatus."** By J. KENT SMITH (*J. Soc. Chem. Ind.* 1899, 18, 213).—The gas passes first through a meter and then into an expansion bottle fitted with an inlet and outlet tube, a thermometer, and a tube attached to a gauge. Before making the actual experiment all air is expelled from the apparatus. In case of high pressure, the gas must be passed through a Dreschel bottle containing a layer of sulphuric acid, and provided with a check clip to regulate the flow. The gas then passes slowly over copper oxide and metallic copper heated to redness in a combustion tube. The products of combustion, water, carbonic, and sulphurous anhydrides, and nitrogen, are collected in a bottle of known capacity filled with water and inverted in an ordinary pneumatic trough; the bottle can be fitted with a rubber stopper carrying a capillary glass top.

When the desired volume of gas has been collected, the stopper, with the tap closed, is inserted into the neck of the bottle under water, and the bottle transferred mouth downwards to an ordinary retort stand. Part of the water is then removed by suction, and strong aqueous soda is run in. This, on shaking, removes the carbonic and sulphurous anhydrides and leaves pure nitrogen. The inverted bottle is placed in an open vessel of water, the stopper is removed, and after a while the bottle slowly raised until the water is at the same level inside and outside. The stopper is then reinserted and the bottle removed and wiped. The water which it contains is carefully measured, and its volume, deducted from the capacity of the bottle, gives the volume of the nitrogen. The usual corrections for temperature, pressure, and aqueous vapour are then made, L. DE K.

**Analytical Methods for Distinguishing Proteid and Amidic Nitrogen.** By JOHN W. MALLET (*Chem. Centr.*, 1899, i, 383; from *Bull.* 54 *U.S. Dept. of Agricult.*).—The author divides the nitrogenous compounds in question into three groups, according to their behaviour with phosphotungstic acid. To the first belong those which give no precipitate, even in concentrated solutions: glycocine, alanine, leucine, asparagine, aspartic acid, tyrosine, and allantoin. The second group includes those which are thrown down in concentrated solutions, but redissolve more or less readily on warming: glutamine, creatine, creatinine, hypoxanthine, carnine, and urea. Peptone gives a precipitate which becomes pasty on heating, and sensibly dissolves, but reappears on cooling. The third group, which yields a precipitate not dissolving on heating, includes egg-albumin, fibrin, casein, legumin, globulin, vitellin, myosin, syntonin, hæmoglobin, albumoses, gelatin, and chondrin.

When calculating the percentage of these substances from the amount of nitrogen yielded by the Kjeldahl-Gunning process, the following factors are proposed: For proteids and related compounds, 6.25; for meat-bases and the more simple animal amides, 3.05; for the more simple amides and amido-acids of vegetable origin, 5.15; and for undigested matters, 9.45.

L. DE K.

**Detection of Hydroxylamine.** By EUGEN BAMBERGER (*Ber.*, 1899, 32, 1805—1806).—One of the best reactions is the conversion of the hydroxylamine into benzhydroxamic acid, which is then tested for by means of the violet-red coloration it gives with ferric chloride; in order to avoid the formation of dibenzhydroxamic acid, it is advisable to use sodium acetate and benzoic chloride instead of sodium carbonate and the chloride as recommended by Lossen. The same test may be used for  $\beta$ -substituted hydroxylamines.

J. J. S.

**Estimation of Hydrazine.** By ENRICO RIMINI (*Gazzetta*, 1899, 29, 265—269).—Potassium iodate reacts with hydrazine sulphate even in the cold, nitrogen being evolved and iodine set free, 12 mols. of iodate being reduced by 15 mols. of hydrazine. The estimation of the hydrazine is carried out by adding to a solution of the sulphate a known volume of a standard solution of potassium iodate. The liquid is then boiled over a flame until it becomes colourless, showing that all the iodine is expelled. After cooling and acidifying with dilute sulphuric acid, the remaining excess of iodate is titrated with sodium thiosulphate in the usual way.

The author regards the reaction as taking place in two stages, hydrogen iodide being first formed, which then reacts with a further quantity of iodate; with bromates, a similar reaction takes place, but only on heating, whilst with chlorates there is no action. Hydroxylamine, phenylhydrazine, and semicarbazide also act on iodates with liberation of iodine.

These results are not in agreement with those obtained by Vitali (*Boll. Chim. Farm.*, April, 1899).

T. H. P.

**Volumetric Estimation of Carbon.** By HENRI IMBERT and P. COMPAN (*Bull. Soc. Chim.*, 1899, [iii], 21, 315—317).—This process is based on the reaction between a sulphuric acid solution of chromic

acid and carbon, yielding chromic sulphate and carbonic anhydride. The unaltered chromic acid used is determined by adding excess of potassium iodide and titrating the iodine liberated with sodium thio-sulphate.

The method of working is as follows: A known weight of the carbonaceous material is evaporated to dryness with an excess of a titrated solution of chromic acid and a little 4 per cent. sulphuric acid. When the liquid becomes syrupy, the colour will be yellow or yellowish-green if the chromic acid be in excess; if, however, the liquid be bluish-green, more chromic acid solution must be added. To the residue, diluted with water, potassium iodide in excess and more 4 per cent. sulphuric acid are added, and the iodine then extracted by shaking up the liquid several times with carbon bisulphide. The iodine solution is then shaken with 5 per cent. sodium hydrogen carbonate solution to neutralise the free acid, after which the liquid is titrated with sodium thiosulphate solution. Test analyses gave satisfactory results.

Hydriodic acid, in presence of hydrobromic acid, can be estimated by adding a cold sulphuric acid solution of chromic acid, which liberates the iodine but not the bromine; the iodine is then extracted with carbon bisulphide, and the solution titrated with thiosulphate solution as described above.

T. H. P.

**New Form of Potash Bulb.** By W. CARRICK ANDERSON (*J. Soc. Chem. Ind.*, 1899, 18, 119).—The apparatus consists essentially of a tube ending in a pear-shaped bulb pierced laterally by four small holes. The latter is surrounded by a larger bulb, sealed to the tube at the top, while from the shoulder of this bulb three narrow-bore tubes pass off laterally, and terminate close to, and at equal distances from, the bottom of a third bulb, which forms the encasement for the apparatus. The two last bulbs are filled about half full with aqueous potash. Owing to the minute subdivision of the gas bubbles, the absorbing power of the alkali is rendered more effective than usual.

L. DE K.

**Absorption of Traces of Carbonic Anhydride in Gaseous Mixtures.** By FÉLIX MABROUTIN, ADRIEN PÉCOUL, and MARIUS BOUYSSY (*Bull. Soc. Chim.*, 1899, [iii], 21, 3—5).—Gautier's experiments (*Abstr.*, 1898, ii, 641) appear to indicate that the last traces of carbonic anhydride in air are not removed by caustic potash solution, and that baryta water must be employed to effect a complete absorption. The authors find, however, that this gas is completely absorbed by passing air through a 2 per cent. solution of caustic potash in such a manner that each bubble remains in contact with the liquid for 15—20 seconds; this result is also attained with a solution of barium hydroxide. After this treatment, 200 litres of air showed no trace of carbonic anhydride; the amount of gas absorbed, when expressed in litres per 100 cubic metres of air, is practically the same, whichever of the two absorbents is employed. The analytical results are tabulated.

G. T. M.

**Decomposition of Silicates by Boric Anhydride.** By PAUL JANNASCH and HERMANN WEBER (*Ber.*, 1899, 32, 1670—1675. Compare Abstr., 1896, ii, 219).—Great difficulty is experienced in converting disthene (kyanite) into a form which is suitable for a complete analysis, since it is not attacked by ammonium fluoride or by boric anhydride under the conditions previously described, and fusion with potassium carbonate does not allow of the estimation of the alkali metals. A complete analysis has been effected by fusing with boric anhydride in the flame of an oxygen coal-gas blowpipe, cooling the crucible with water, dissolving the glassy mass by means of a solution of hydrogen chloride in methylic alcohol ("Salzsäure-methylester"), and evaporating three or four times with this solution to remove the whole of the boric acid.

Analyses are given of, I, disthene from Lincoln county, N. Carolina; II, quartz porphyry from the Kinzigthal:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
37·16		60·89		0·33		1·35	0·46		100·19
71·76	trace	16·58	1·75	0·67	0·83	5·04	0·52	2·60	99·75

Topaz, and other minerals containing fluorine, can be analysed by boric anhydride fusion, since the whole of the fluorine is eliminated as boron fluoride, and not as silicon fluoride. Topaz, like disthene, is only attacked by using an oxygen coal-gas blowpipe. Two analyses gave SiO<sub>2</sub> = 33·39 and 33·35 per cent. T. M. L.

**Quantitative Analysis without using Hydrogen Sulphide.** By A. RAWITSCH (*Chem. Centr.*, 1899, i, 376—377; from *J. Russ. phys.-chem. Ges.*, 30, 761—767).—The process resembles in principle the one proposed by Bischoff in 1862. After removing silver, mercurous mercury, and the bulk of the lead by hydrochloric acid, the neutralised liquid is heated with excess of yellow ammonium sulphide. The solution then contains the alkalis and the alkaline earths in addition to the tin-arsenic group, which may be precipitated by addition of hydrochloric acid.

The precipitate insoluble in ammonium sulphide is treated with dilute hydrochloric acid, which dissolves the sulphides of zinc, manganese, iron, and the hydroxides of aluminium and chromium, and also any phosphates of the alkaline earths. These must be separated as usual. The matter insoluble in hydrochloric acid is digested with nitric acid, which leaves the mercury sulphide undissolved; after expelling the excess of acid, the liquid is diluted, and the bismuth precipitated with ammonium chloride as bismuth oxychloride. The neutralised filtrate is then mixed with a little sodium thiosulphate, and a few drops of hydrochloric acid and boiled; copper and cadmium are precipitated as sulphides, whilst nickel and cobalt remain dissolved.

L. DE K.

**Estimation of Gold and its Separation from Platinum and Iridium.** By LUDWIG VANINO and L. SEEMANN (*Ber.*, 1899, 32, 1968—1972).—The method recommended is the reduction of gold chloride to metallic gold by hydrogen peroxide in the presence of sodium or potassium hydroxide. Even in the cold, the reaction is complete in a



few minutes, whereas the usual methods require 2—12 hours. When very dilute solutions are employed, it is advisable to warm the mixture for a short time after reduction, and then to add hydrochloric acid, as by this means the precipitate is rendered easier to filter; in no case must the hydrochloric acid be added until the excess of hydrogen peroxide has been destroyed by warming. The method cannot be employed for the estimation of gold in sodium aurichloride.

The same reaction may be employed as a qualitative test, as it is extremely delicate; 10 c.c. of a solution containing 0.00003 gram of gold, gives a slight red colour, with a bluish shimmer.

As platinum and iridium salts are not reduced in the cold by hydrogen peroxide and alkali, the reaction affords a simple method for the separation of gold from these two metals. J. J. S.

**Colorimetric Estimation of Phosphoric Acid in Water.** By ADOLF JOLLES (*Chem. Centr.*, 1899, i, 375; from *Arch. Hyg.*, 34, 22—30).—The process is based on the yellow coloration produced when phosphates are heated with a nitric acid solution of potassium molybdate; the process is, of course, applicable only in very dilute solutions, as a solution containing more than 0.001 gram of phosphoric acid in 20 c.c. becomes turbid when heated at 80° with the reagent.

When testing waters, it is necessary to evaporate the water to dryness with a little nitric acid, and to heat for some time at 130° in order to render the silicic acid insoluble; the residue is then taken up with dilute nitric acid, filtered, and diluted to a suitable volume, of which 20 c.c. is used for the test.

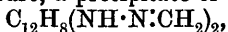
The reagent is made by dissolving 8 grams of pure potassium molybdate in 50 c.c. of colourless nitric acid of sp. gr. 1.2; 1 c.c. of this solution precipitates 0.001 gram of phosphoric anhydride. The liquid for comparison is prepared by dissolving 53.23 grams of recrystallised disodium hydrogen phosphate in water, and diluting to 1 litre; before use, this solution must be further suitably diluted. L. DE K.

**Examination of Commercial Amylic Alcohol.** By HENRY DROOP RICHMOND and F. R. O'SHAUGHNESSY (*J. Soc. Chem. Ind.*, 1889, 18, 107—109).—The amylic alcohol to be used in the Leffmann-Beam process, or in Gerber's modification of that method, should have a sp. gr. 0.8145 to 0.816 at 15.5°. The boiling point should not exceed 130.5°, at which temperature 23.5 c.c. should distil over from 25 c.c. of the alcohol; 10 c.c. should give a clear and but slightly-coloured liquid on addition of 10 c.c. of hydrochloric acid of sp. gr. 1.17, and the addition of 1.5 c.c. of water should cause a permanent turbidity. Tables are given for the correction of the density when taken at temperatures differing from 15.5°, and another table gives the density, boiling points, polarisation, and solubility of 14 samples of commercial amylic alcohol. L. DE K.

**Areometric Estimation of Dextrose in Urine.** By THEODOR LOHNSTEIN (*Chem. Centr.*, 1899, 391; from *Allg. Med. Central Zeit.*, 1898, 58).—The author has improved the process proposed by

Schlosser (this vol., ii, 185) which itself is a modification of the original method recommended by Roberts. The new process is as follows: 100 c.c. of urine, if containing much sugar, are fermented with 4 c.c. of yeast, but if the copper test shows but little sugar, 1 c.c. is sufficient; a little of the urine is first put into a graduated tube and after adding sufficient yeast to increase the volume by 4 c.c., the contents and the remaining urine are put into the fermentation flask. After fermenting for 12 hours at 35–40°, the clear liquid is poured off and its sp. gr. taken; 100 c.c. of the original sample is then mixed with 1.6 c.c. of a 1 per cent. solution of salt, and its sp. gr. is also taken at the same temperature. The difference in the two densities multiplied by 233 (or 230 if only 1 c.c. of yeast has been used) gives the amount of dextrose. L. DE K.

**Detection and Estimation of Formaldehyde.** By CARL NEUBERG (*Ber.*, 1899, 32, 1961–1964).—When aqueous solutions of paradiphenyleneparadihydrazine hydrochloride (*Abstr.*, 1887, 958) and formaldehyde are mixed and allowed to remain for a few minutes at the ordinary temperature, a precipitate of the *hydrazone*,



is thrown down in the form of slender needles; it turns orange-coloured at 166°, sinters at 202°, and melts at about 220°, is insoluble in all the ordinary solvents, and is readily decomposed by glacial acetic acid or mineral acids. It is instantaneously deposited in the pure form as a flocculent precipitate, when a colourless solution of the hydrochloride is slowly added to slightly more than the theoretical quantity of 40 per cent. formaldehyde solution at 60°. A solution of formaldehyde of 1 part per 5000 gives the reaction distinctly. Although not so delicate as Jorissen's phloroglucinol test or Lebbin's resorcinol test, it has the advantage that it serves to distinguish between formaldehyde and furfuraldehyde, or other aldehydes and ketones, since the corresponding hydrazones of all these are soluble in alcohol.

In the quantitative estimation, the aldehyde solution (1–2 parts per 1000) is added gradually to the warm aqueous solution of the hydrochloride and the hydrazone filtered, washed with hot water, alcohol, and pure ether, dried at 90°, and weighed. Or if no substance except formaldehyde is present which reacts with iodine and thiosulphate, the hydrazone may be filtered off and the excess of hydrazine estimated in the filtrate by Meyer's method (*Abstr.*, 1887, 1042), or, still better, Blank and Finkenberger's method (this vol., ii, 188) for the estimation of formaldehyde can be employed. J. J. S.

[**Estimation of Glycerophosphoric Acid.**] By JACQUES CAVALIER and POUGET (*Bull. Soc. Chim.*, 1899, [iii], 21, 364–366).—See this vol., i, 660.

**Estimation of Salicylic Acid.** By WILHELM FRESSENIUS and LEO GRÜNHUT (*Zeit. anal. Chem.*, 1899, 38, 292–301).—The authors have submitted to a critical investigation three methods of estimating salicylic acid, namely, (1) extraction with volatile solvents and weighing the residue from the evaporated extract; (2) an iodimetric process;

(3) Freyer's bromine absorption method (Abstr., 1897, ii, 608). The last alone gave satisfactory results. The first method failed in consequence of the volatility of salicylic acid, it being found impossible to expel the solvent (chloroform, ether, or light petroleum and ether) completely, either at 100° or at a lower temperature, without serious loss of salicylic acid. The second method gave very uncertain results, and the authors were unable to confirm the statement of Messinger and Vortmann (Abstr., 1890, 1473) that 1 mol. of salicylic acid consumes 6 atoms of iodine. The bromination method proceeds in accordance with the equations,  $C_6H_2 \cdot OH \cdot COOH + 8Br = C_6HBr_3 \cdot OBr + 4HBr + CO_2$ , and  $C_6HBr_3 \cdot OBr + 2KI = C_6HBr_3 \cdot OK + KBr + I_2$ , so that ultimately 6 atoms of halogen are consumed by one molecule of salicylic acid. At least 75 per cent. excess of bromine (in the form of an acidified mixture of bromate and bromide) must be used, and stronger solutions than were employed by Freyer are advisable. For 0.2 gram of sodium salicylate, there should be taken 100 c.c. of a solution containing 3 grams of sodium bromate and 20 grams of sodium bromide per litre. This, diluted with 300 c.c. of water, is first acidified with 30 c.c. of hydrochloric acid of sp. gr. 1.1. The 1 per cent. solution of the salicylate is then added with stirring, and after waiting for 5 minutes 30—40 c.c. of 10 per cent. potassium iodide solution is added and the free iodine titrated by thiosulphate. It is important not to add starch paste until the liquid is nearly decolorised. To estimate salicylic acid in presence of starch, it is necessary to separate the latter by dissolving in 90 per cent. alcohol and to employ an aliquot part of the filtered solution. M. J. S.

**Delicate Test for Gallic Acid, Serving to Distinguish it from Digallic Acid and Pyrogallol.** By GIOACHINO GRIGGI (*Chem. Centr.*, 1899, ii, 454; from *Boll. Chim. Farm.*, 38, 5—6).—If to a 1 per cent. solution of gallic acid is added 1 c.c. of a solution of potassium cyanide (1 : 30), a clear, ruby-red coloration is developed which fades after a time, but is regenerated when the mixture is vigorously shaken; the same effect is obtained by adding hydrogen dioxide.

Digallic acid and pyrogallol give a yellowish-red colour with potassium cyanide. On adding hydrogen dioxide, the pyrogallol mixture turns yellowish-brown, whilst the digallic acid mixture gives a dirty white precipitate. L. DE K.

**Valuation of "Saccharin."** By E. EMMET REID (*Amer. Chem. J.*, 1899, 21, 461—471).—Orthobenzoic sulphinide is hydrolysed by heating at 100° with 71 per cent. sulphuric acid during three hours or by boiling with dilute hydrochloric acid during two hours and then evaporating nearly to dryness; parasulphamidobenzoic acid is not hydrolysed under these conditions, but is completely hydrolysed when heated with concentrated sulphuric acid at 230—260° during several hours; neither compound is hydrolysed by boiling with caustic soda.

For the valuation of "saccharin," it is best to hydrolyse with hydrochloric acid, as the sulphinide is more completely hydrolysed, whilst the parasulphonamide, which liberates traces of ammonia when sulphuric acid is used, is not attacked at all by the hydrochloric acid.

The method of analysis is as follows: 0.650 gram "saccharin" is weighed into a 100 c.c. Florence flask and 50 c.c. of dilute hydrochloric acid (1 : 8) are added; the flask is gently boiled on a sand-bath for two hours with a reflux tube, and the contents are then allowed to boil down to 10 c.c.; the solution is diluted, transferred to a distilling flask, made alkaline with 10 grams of sodium hydroxide dissolved in 20 c.c. of water, the ammonia is carried over by a current of steam into 25 c.c. of standard acid, about  $N/7$ , and the excess of acid titrated with standard potassium hydroxide, using cochineal as an indicator.

It is shown that five different classes of nitrogen compounds can be separately estimated in one analysis, thus (1) ammonium salts by distilling with magnesia; (2) unstable amides such as paranitrobenzamide by distilling with caustic soda; (3) orthobenzoic sulphinide by heating with hydrochloric acid and again distilling with caustic soda; (4) parasulphaminobenzoic acid by heating with sulphuric acid and distilling with caustic soda; and (5) other nitrogen compounds by Kjeldahl's method.

T. M. L.

**Estimation of Fat in Milk.** By M. KÜHN (*Chem. Centr.*, 1899, i, 388—389; from *Milch-Zeit.*, 27, 807—808, 823—825, 835—837).—A thorough investigation has been made as to the merits of Soxhlet's areometric process for the estimation of fat in milk; this process consists in determining the sp. gr. of ether before and after agitating with alkaline milk; the difference in gravity is then a measure of the amount of fat.

The author recommends the process, but points out a few important facts. Ether saturated with water such as is wanted in this process, does not keep well, alcohol being gradually formed to some extent; the ether should therefore be re-agitated with water containing a little potassium hydroxide just before use. Another occasional source of error is the inaccuracy of the hydrometers employed. L. DE K.

**Apparatus for Rapid Analysis of Milk.** By GEORGE D. MACDOUGALD (*J. Soc. Chem. Ind.*, 1899, 18, 235—238).—The author's process is, chemically, that of Leffmann-Beam, but the apparatus, which is fully illustrated in the paper, and which cannot be properly explained without reproducing the drawings, is quite different, and is specially devised to enable a large number of samples to be accurately analysed in a short time. For instance, the well-known Leffmann-Beam bottle is replaced by a kind of U-tube provided with a pear-shaped bulb to hold the mixture of milk and acid. After the milk has been introduced, the amyl alcohol, or a mixture of it with hydrochloric acid, is added from a specially-constructed bottle, and the sulphuric acid is also introduced by means of an apparatus consisting of a series of tubes, or calibrated bulbs, fed by a tube common to all. The mixing is done by drawing air through the bulb by means of an aspirator, and, to facilitate the rising of the fat, a mixture of sulphuric acid and water of higher sp. gr. than the mixture of milk and acid is added, so as to occupy the lower part of the bulb.

The tube is calibrated by means of milk the percentage of fat of which has been carefully determined, say, by Adams' method. The

tubes are whirled in a special apparatus, allowing the use of a steam-bath. Three minutes is ample for 500—600 revolutions, but at higher speeds the time may be shortened. The fat is read off by placing each bulb in a lantern, the image being projected on to a scale.

L. DE K.

**Detection of Arachis Oil in Olive Oil.** By M. VIERTH (*Chem. Centr.*, 1899, i, 383—384; from *Pharm. Zeit.*, 43, 924).—The author agrees with Tortelli and Ruggeri (*Abstr.*, 1898, ii, 653) that the only trustworthy test for the presence of arachis oil in olive oil is the melting point of the isolated arachidic acid.

Thirty grams of the sample is saponified with 12 per cent. alcoholic potash, the fatty acids are liberated by means of hydrochloric acid, and then dissolved in warm 90 per cent. alcohol. This solution is precipitated with alcoholic solution of lead acetate, and the precipitate is extracted with ether. The insoluble mass is then decomposed with hydrochloric acid, and the fatty acids dissolved in excess of warm 90 per cent. alcohol. When cold, the arachidic acid crystallises out, and is collected on a filter and washed with cold alcohol; it is then dissolved in boiling alcohol, evaporated in a tared dish and weighed, allowance being made for the slight solubility in cold alcohol.

The melting point should be  $71^{\circ}$ , but it will be necessary to carefully recrystallise several times from hot alcohol before a satisfactory result can be obtained.

L. DE K.

**Analysis of Aniline Oils and Aniline Salt.** By ADOLF LIEB-MANN and ARTHUR STUDER (*J. Soc. Chem. Ind.*, 1889, 18, 110—112).—*Estimation of Water in Aniline Oil.*—100 c.c. of the sample are distilled and 10 c.c. collected in a narrow, graduated measure holding 15 c.c.; 1 c.c. of brine is added, the whole is well shaken, and left to settle. The increase in volume of the brine, + a correction of 0.3 c.c., gives the amount of water.

The boiling is now continued, and the temperature is observed in intervals of 10 c.c.; 80 per cent. of the oil should boil within  $0.5^{\circ}$ . *Specific gravity.*—This should be taken with the distillate after the water has been removed; good oils have a sp. gr. from 1.0265—1.0270 at  $15^{\circ}$ . *Sulphur compounds.*—These are found to be given off as hydrogen sulphide on boiling. The sample is therefore boiled for some hours in a reflux apparatus, while a current of carbonic anhydride is passed through, carrying the evolved hydrogen sulphide into a measured quantity of  $N/10$  silver nitrate; at the end of the operation, the silver sulphide is removed, and the silver remaining in the solution estimated; from the loss, the amount of sulphur is calculated.

*Solubility in Dilute Hydrochloric Acid.*—This is the most important test, as it reveals the presence of objectionable non-basic substances, such as nitrobenzene or naphthalene. For the detection of ortho- or para-toluidine, the authors use Reinhardt's method (*Abstr.*, ii, 608), with only a very slight modification. This process consists in dissolving the sample in hydrobromic acid and adding standard solution of mixed potassium bromide and bromate until the liquid contains free bromine. Another portion of the sample is dissolved in dilute hydrochloric acid and precipitated with oxalic acid, which combines

with the paratoluidine and the aniline. These may then be recovered from the washed precipitate by means of warm aqueous potash, and then weighed and again titrated with bromine. As aniline absorbs 3 mols. of bromine, whilst the toluidines only absorb 2 mols., the respective amounts of aniline and toluidines may be readily calculated. The authors find that pure aniline may be dissolved in hydrochloric acid, but that for mixtures, the use of hydrobromic acid is necessary; or a properly made mixture of hydrochloric acid and potassium bromide may be substituted. Instead of using iodide starch-paper as indicator, they estimate the small excess of bromine added by means of potassium iodide and sodium thiosulphate, using starch-water as indicator.

*Analysis of Aniline Salt.*—The sample may be conveniently analysed by Reinhardt's bromine process, the appearance of the sample being of great value to an expert. Water is estimated by drying for 24 hours in a desiccator. As the presence of free acid is of serious importance, the authors estimate it as follows: 5 grams of the salt are dissolved in 10 c.c. of water, and 5 drops of crystal violet (1:1000) added, and the mixture compared with a similarly made solution of aniline salt free from acid. If now the sample shows acidity—namely, a bluer or even a green shade—a decinormal aqueous solution of aniline is run in until the colours are exactly alike, and the amount of free acid is readily found by calculation. L. DE K.

*Estimation of Alkaloids by Iodine Solution.* By MAX SCHOLTZ (*Zeit. anal. Chem.*, 1899, 38, 278—280. See Abstr., 1896, ii, 282, 682; this vol., ii, 390, 534).—In reply to Kippenberger's contention that the difference between the author's results and his own is due to a difference in the amount of potassium iodide in their respective solutions, the author states that he employed the usual *N*/20 iodine solution containing 10 grams of potassium iodide per litre, but points out that in consequence of the different molecular weights of the alkaloids a different absolute weight of iodide in each case would be associated with an uniform molecular addition of iodine, if one and the same solution were employed for all, and would, moreover, vary with every change in the proportion of iodine solution added.

M. J. S.

*Estimation of Alkaloids by Iodine Solution.* By CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1899, 38, 280—287. See preceding abstract).—The author shows that when the conditions have been similar, Scholtz has obtained results agreeing with his own, but maintains that Scholtz has used an iodine solution containing more potassium iodide than is suitable for the present purpose. Since in the course of an analysis the alkaloids would be obtained and weighed in a state of approximate purity, it is easy to prepare from a standard specimen a solution of nearly the same concentration as the one to be titrated, and to standardise the iodine solution therewith, and so titrate the product of the analysis under identical conditions. M. J. S.

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## General and Physical Chemistry.

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**Diffusion of Light by Solutions.** By WALTÈRE SPRING (*Rec. Trav. Chim.*, 1899, 18, 233—246).—Solutions of the chlorides, bromides, chlorates, and nitrates of sodium, potassium, ammonium, barium, and calcium were placed in a small, spherical flask, clarified by adding a few drops of a colloidal solution of ferric, or better still, cadmium or zinc, hydroxide, and allowing the precipitated hydroxide to settle (this vol., ii, 537); the flask was then placed in the cone of light from a powerful electric lantern, so that the apex of the cone coincided with the centre of the flask (compare Picton and Linder, *Trans.*, 1892, 143); in no case was there a visible cone of light within the flask. Solutions of salts of the earthy or heavy metals cannot be clarified in this way, as they react with hydroxides to form basic salts; they can only be compared with distilled water in respect of their power of diffusing light. The chlorides, chlorates, sulphates, and nitrates of zinc, cadmium, manganese, cobalt, and nickel do not exhibit a cone appreciably more distinct than that obtained with distilled water; on the other hand, the neutral solutions of salts of aluminium, chromium, iron, copper, mercury, and lead, especially the chlorides of the first metals, exhibit a very marked cone. If a little of the corresponding metallic hydroxide is dissolved in the solution of the chloride of iron, aluminium, zinc, cadmium, or mercury, the cone becomes still more marked, the addition of a few drops of hydrochloric acid causing it to disappear, however; with the chlorides of copper, nickel, and cobalt, no such result is obtained. It will be noted that the salts of which the solutions exhibit no cone are just those which are largely dissociated into their ions, and which contain metals that form hydroxides more or less soluble in water. The salts which exhibit a cone are those which are known to undergo electrolytic hydrolysis to a certain extent, and of which the metals form hydroxides insoluble in water; the appearance of the cone is probably due to the presence of a small quantity of the hydroxide in colloidal solution.

Dilute solutions of certain indisputably colloidal substances were examined, and all found to exhibit a very marked cone; such are aqueous solutions of gelatin, gum arabic, and dextrin in water; of colophony, Canada balsam, and gum-lac in alcohol; also solutions of sodium soap, alkali silicates (dilute), Williamson's blue, Prussian blue, and phenyl blue. If there is any suspicion that the appearance of a cone may be due to fluorescence, a yellow screen is interposed in the path of the beam of light; if the cone persists, it was due, in part at any rate, to diffusion; if it vanishes, it was due to fluorescence, which is occasioned only by the more refrangible rays. Magenta and vesuvine (phenyl-brown) exhibit a marked cone in aqueous solution; their solutions in alcohol, however, give no more pronounced a cone than alcohol itself does. Tannin and sodium soap both give a very marked cone in aqueous solution; the latter in alcohol-ether solution

exhibits no cone except such as is due to fluorescence, whilst tannin in acetic acid solution gives a cone that is in part due to fluorescence, but appears to be due in part to diffusion. C. F. B.

**An X-Ray Photometer.** By ALEXANDRE HÉBERT and GEORGES REYNAUD (*Bull. Soc. Chim.*, 1899, [iii], 21, 392—394).—For the purpose of studying the absorption of Röntgen rays by different liquids, a modified form of the Duboscq colorimeter has been devised. The instrument is supported on a wooden stand, and in place of the mirror a vacuum tube is arranged underneath. The liquids, absorbing powers of which are to be compared, are contained in two cylinders placed side by side, the depths of the liquid layers being varied by means of hollow glass pistons, the displacements of which can be read off on a vertical scale. The lower faces of the pistons are covered with fluorescent discs, the platinocyanide being uppermost; gutta-percha coatings protect the discs from the action of the liquids in which they are immersed. The pencils of light emitted by the fluorescent discs are brought into contact in the ordinary way by means of reflection from the interior faces of two glass parallelipedons. The field thus consists of two halves, which are made of equal intensity by varying the positions of the pistons. T. H. P.

**Specific Absorption of X-Rays by Metallic Salts.** By ALEXANDRE HÉBERT and GEORGES REYNAUD (*Bull. Soc. Chim.*, 1899, [iii], 21, 394—402).—By means of the instrument described in the preceding abstract, the absorption of Röntgen rays by solutions of a large number of metallic salts has been studied. One of the cylindrical tubes was filled with distilled water and its piston kept in a fixed position, and in the other was placed the salt solution containing the gram-molecular weight (or, in some cases, a simple multiple or sub-multiple of it) per litre. The piston in the second cylinder being adjusted to give equal luminosity of the two halves of the field, the difference between the heights of the two pistons gives the length of a column of water having an absorption equal to that caused by the salt. On examining in this way different metallic salts of the same acid, it is found that, in general, the absorption increases with an increase in the atomic weight of the metal; further, the numbers obtained seem to divide the metals into a number of groups, the salts of the members of any one group having approximately the same molecular absorption. For instance, in the case of the metallic chlorides: those of hydrogen, lithium, and sodium give numbers varying from 11.8 to 15.5 (compared with a column of distilled water 41.5 mm. in height); those of potassium, ammonium, magnesium, and calcium have values lying between 23.5 and 25.9, that is, about double those of the first group; those of iron, manganese, copper, cobalt, zinc, and nickel have numbers ranging from 33.1 to 34.8, or about treble those of the first group; and for the heavy metals, chromium, barium, strontium, cadmium, gold, tin, platinum, and mercury, the limiting values are 37.3 and 40.1. On arranging the metals according to the absorptions of their nitrates, an almost identical series is obtained. A similar classification into groups is noticed for salts containing the same metal but different acids; in this case also, it is approximately



true that the absorption of a salt increases with the molecular weight of the corresponding acid.

T. H. P.

**Aqueous Solutions of Double Salts. II. Chlorides.** By HARRY C. JONES and KENJIRO OTA (*Amer. Chem. J.*, 1899, 22, 5—14. Compare Jones and Mackay, *Abstr.*, 1897, ii, 396).—The authors' experiments show that the conductivity of aqueous solutions of the double chlorides  $2\text{KCl}\cdot\text{ZnCl}_2$ ;  $\text{KCl}\cdot\text{CdCl}_2$ ;  $\text{NaCl}\cdot\text{AlCl}_3$ , and  $2\text{NH}_4\text{Cl}\cdot\text{HgCl}_2$ , tends, with increasing dilution, to become equal to the sum of the conductivities of the constituent salts; it thus appears that, with infinite dilution, complete dissociation of the double chloride into its constituents would occur. In concentrated solution, however, the observed conductivities are much lower than those calculated for complete dissociation into the constituent salts; this indicates that the double chlorides named are, to some extent, capable of existing as such in concentrated solutions, and confirms Remsen's view, that the double chlorides are definite chemical compounds. A similar conclusion was formerly drawn by Jones and Mackay (*loc. cit.*) in the case of some of the alums, but owing to the ease with which these undergo complete dissociation in aqueous solution, the results were less well defined than those now recorded.

Under the same conditions of concentration and temperature, the zinc potassium chloride is much less dissociated than the corresponding cadmium salt, and this, in turn, less than the aluminium sodium or the ammonium mercury double salts.

W. A. D.

**Electrolysis of Ammonium Thiosulphate.** By PAUL PIERRON (*Bull. Soc. Chim.*, 1899, [iii], 21, 477—481).—Ammonium sulphide is the only product obtained at the cathode, whilst at the anode, sulphur with various proportions of sulphurous, sulphuric, trithionic, and tetrathionic acids are formed. The amounts of sulphur and sulphuric acid increase, whilst that of tetrathionic acid decreases, as the current increases.

R. H. P.

**Magnetic Properties of the Elements.** By STEFAN MEYER (*Monats.*, 1899, 20, 369—382).—The magnetic susceptibility of a number of the elements, partly in the form of powder, partly in larger pieces, has been determined. The coefficient of susceptibility for each element, when divided by the number of gram-atoms per litre, gives the atomic magnetism. A table is drawn up showing the atomic magnetism for each element, and embracing the numbers given by Königsberger (*Ann. Phys. Chem.*, 1898, [ii], 66, 732), as well as those obtained by the author. It appears that a general relation exists between the susceptibility of the elements and their atomic weights.

J. C. P.

**Thermal Properties of Normal Pentane.** By J. ROSE-INNES and SYDNEY YOUNG (*Phil. Mag.*, 1899, [v], 47, 353—367).—The relations of temperature, pressure, and volume have been determined for normal pentane by the methods previously employed in the case of isopentane (*Proc. Phys. Soc.*, 13, 602—657). The equation  $p = bT - a$  at constant volume holds for a wide range of volumes; as in the case of isopentane, the deviations are greatest at intermediate volumes.

For each volume there is one, and only one, temperature at which the gas has its pressure equal to that required by the laws of a perfect gas, this temperature  $T$  being given by the expression  $a/(b - R/v)$ . When  $v$  is greater than 8, the values of  $T$  for normal pentane are fairly constant, the mean being  $838.5^\circ$ ; the corresponding temperature for isopentane was  $842.4^\circ$ .

The variations of  $b$  and  $a$  with the temperature have been studied. When the quantity  $1/av^2$  is plotted against  $v^{-1}$ , a discontinuity is found about the volume 3.4, the point where the corresponding curve for isopentane was discontinuous. The value of  $1/av^2$  is always smaller for normal pentane than for isopentane at the same value of  $v$ ; the difference diminishes as the volume increases. Thus, if the pressure is expanded in ascending powers of the density, the coefficient of the second power is different for the two isomerides.

J. C. P.

**Determination of the Solidifying Point.** By AL. A. SHUKOFF (*Zeit. angew. Chem.*, 1899, 563—564).—The apparatus is a modification of Eykmann's apparatus for cryoscopic determinations. It consists of a cylindrical vessel 3 cm. wide and 11 cm. high, which has been sealed into another 5 cm. wide. In the interspace between the two vessels a Crookes' vacuum has been made, the inner vessel thus being surrounded by a Dewar's vacuum jacket.

The determination of the solidifying point is conducted by partially filling the inner vessel with the clear melted substance; a thermometer showing fifths of a degree is then introduced through a perforated cork until its bulb reaches the centre of the liquid. When the temperature is about  $5^\circ$  above the expected solidifying point the apparatus is continually and strongly shaken up and down until the mass has become opaque. According to the nature of the substance, the temperature remains constant for some time (paraffin), or it begins to rise and then remains constant for some time (fats). This constant point is then recorded as the solidifying point.

L. DE K.

**Heat of Oxidation of Sodium.** By ROBERT DE FORCRAND (*Compt. rend.*, 1899, 128, 1449—1452).—According to Beketoff (*Abstr.*, 1884, 1247, and 1888, 1244),  $\text{Na}_2\text{O sol.} + \text{Aq} = \text{Na}_2\text{O diss.}$  develops 54.766 Cal. and  $\text{K}_2\text{O sol.} + \text{Aq} = \text{K}_2\text{O diss.} + 67.40$  Cal. Combining these values with the heats of reaction of sodium and potassium with water for which the means of the determinations of Thomsen and Joannis are taken, there is obtained:  $\text{Na}_2\text{ sol.} + \text{O gas} = \text{Na}_2\text{O sol.} + 100.084$  Cal. and  $\text{K}_2\text{ sol.} + \text{O gas} = \text{K}_2\text{O sol.} + 94.90$  Cal. As this is the only case in which the heat of formation of a sodium compound is greater than that of the corresponding potassium compound, the author has revised Beketoff's numbers. His method is to dissolve mixtures of known composition of  $\text{Na}_2\text{O}$  and  $\text{Na}_2\text{O}_2$  in dilute hydrochloric acid; from the measurement of the heat evolved and a knowledge of the heat of solution of the peroxide, the heat of solution of  $\text{Na}_2\text{O}$  is obtained. The mean value found is:  $\text{Na}_2\text{O sol.} + \text{Aq} = \text{Na}_2\text{O diss.} + 63.865$  Cal., a number considerably higher than Beketoff's. From this,  $\text{Na}_2\text{ sol.} + \text{O gas} = \text{Na}_2\text{O sol.} + 90.985$  Cal., which is less than the corresponding number for potassium.

T. H. P.

**The Oxides of Sodium and the Chemical Function of Water compared with that of Hydrogen Sulphide.** By ROBERT DE FORCRAND (*Compt. rend.*, 1899, 128, 1519—1522. Compare this vol., ii, 95).—From the equations  $\text{H}_2\text{O sol.} + \text{Na sol.} = \text{H gas} + \text{NaOH sol.} + 31.19 \text{ Cal.}$ , and  $\text{NaOH sol.} + \text{Na sol.} = \text{H gas} + \text{Na}_2\text{O sol.} - 11.685 \text{ Cal.}$ , it is seen that the quantities of heat developed during the successive replacement by sodium of the hydrogen atoms in the water molecule differ by 42.875 Cal., which is an abnormally large difference. The corresponding heat changes for the action of sodium on hydrogen sulphide are 44.45 and 31.80 Cal., giving a difference of 12.65, and a mean value of 38.12. When the hydrogen atoms of the hydroxyl groups of catechol are successively replaced by sodium, the amounts of heat developed are 43.61 and 33.08 respectively, the difference being 10.53, and the mean 38.34; the action of sodium on phenol develops 38.42 Cals. From these numbers, the author concludes that hydrogen sulphide, considered thermally, is a true diphenol with the formula  $\text{H-S-H}$ , but that water is not a symmetrical compound and must be represented by the formula  $\text{H-OH}$ . T. H. P.

**Determination of the Heats of Combustion of some Organic Compounds.** By B. ZOUBOFF (*Chem. Centr.*, 1899, i, 586—587; from *J. Russ. Chem. Soc.*, 1898, 30, 926—950).—The heats of combustion of the following organic compounds were determined by Berthelot's calorimetric method. In calculating the kilogram-calories per gram—

	As liquids.		As gases.
	At constant volume.	At constant pressure.	At constant pressure.
Octane .....	1310.7	1313.4	1328.4
Decane .....	1621.1	1624.3	1644.5
Trimethylethylene .....	801.0	802.5	(807.8)
Hexylene .....	958.7	960.5	—
Hexamethylene .....	942.2	943.9	—
Methylpentamethylene .....	943.9	945.6	—
Propylic alcohol .....	483.6	484.4	497.2
Isopropylic alcohol .....	477.9	478.7	490.8
Butylic alcohol .....	642.5	643.7	658.8
Isobutylic alcohol .....	639.8	640.9	655.5
Tertiary butylic alcohol .....	633.3	634.4	647.7
Fermentation amylic alcohol .....	769.5	798.0	814.9
Dimethylethylcarbinol .....	789.3	790.7	805.4
Heptylic alcohol .....	1111.7	1113.8	(1137.9)
Methylethylketone .....	586.3	587.1	596.9
Methylpropylketone .....	739.5	740.6	(752.1)
Methylisopropylketone .....	738.8	739.9	750.9
Diethylketone .....	740.5	741.6	753.3
Methylbutylketone .....	901.0	902.5	916.7
Pinacolone .....	897.6	899.1	(912.1)
Dipropylketone .....	1057.3	1059.1	1075.5
Methylhexylketone .....	1212.9	1215.0	1235.3
Dimethylic carbonate .....	343.5	343.5	354.3
Diethylic carbonate .....	652.5	653.1	667.6

molecule of substance, Bartoli and Stracciati's data (compare also *J. Russ. Chem. Soc.*, 1898, 30, 946) for the specific heat of water, and Luginin's determinations of the specific and latent heats of evaporation of the various compounds, have been employed. In the cases, however, where the figures are in brackets, the latter constants were calculated from those of analogous compounds. The heats of combustion of isomeric compounds of the same series are not identical. In the original paper, the numbers obtained by the employment of Regnault's determinations of the specific heat of water at 20° are also quoted and are slightly higher than those on p. 589. E. W. W.

**Cryoscopic Measurements.** By FRANÇOIS MARIE RAOULT (*Bull. Soc. Chim.*, 1899, [iii], 21, 610—612).—A reply to Ponsot's criticisms (this vol., ii, 546) of the author's work. T. H. P.

**Temperatures of Maximum Density of Aqueous Solutions of Alkali Chlorides.** By LOUIS C. DE COPPET (*Compt. rend.*, 1899, 128, 1559—1561).—By the method previously described by the author (Abstr., 1895, ii, 343), the temperature of maximum density of a number of solutions of different strengths of potassium, sodium, lithium, and rubidium chlorides have been measured. The difference between the temperatures of maximum density of the solution and of pure water, divided by the number of gram-molecules of the chloride per litre of solution, is termed the molecular depression of the temperature of maximum density, and in the case of solutions of potassium chloride it apparently decreases slightly as the concentration increases. For solutions of sodium and rubidium chlorides, no regular change of this molecular depression with the concentration can be traced, but with lithium chloride, an increase in the concentration corresponds with an increase in the molecular depression of the maximum density temperature, and the value of this latter is only about one-half the values for the other alkali chlorides. T. H. P.

**Dissociation of Gases under Constant Pressure and in presence of an Excess of one of the Products of Dissociation.** By RUDOLF WEGSCHEIDER (*Monats.*, 1899, 20, 307—319).—For a gas which dissociates into two simpler molecules, the equation of equilibrium, when the pressure is taken as constant, leads to the result  $\alpha_\infty = a^2$ , where  $\alpha_\infty$  and  $a$  are the degrees of dissociation, (1) when an infinitely large excess, (2) when no excess, of either product is present. Thus, as the excess of one of the products of dissociation increases, the degree of dissociation falls until it reaches the limiting value given by the above equation. In more complicated cases, the degree of dissociation in presence of an excess of one product depends on the relative number of molecules concerned. Similar relations hold for solutions: when a reaction in dilute solution is accompanied by a change in the osmotic pressure, further dilution shifts the equilibrium in the direction of increased osmotic pressure.

In the light of the relation  $\alpha_\infty = a^2$ , the author discusses the experiments of Wurtz on the dissociation of phosphorus pentachloride, and concludes that this substance, which was supposed to be undissociated in presence of a large excess of phosphorus trichloride, was in reality dissociated to the extent of 3—10 per cent. J. C. P.

**Dissociation of the Hydrochloride of Methylic Ether.** By RUDOLF WEGSCHEIDER (*Monats.*, 1899, 20, 320—335).—The author reviews Friedel's work on the dissociation of the compound  $\text{OMe}_2\text{HCl}$ , and calculates the equilibrium constant for each of his experiments. With the help of the most consistent of Friedel's numbers, the formula  $\log 10^5 K_c = -1078.061/T + 4.71704$  is obtained; the values of  $K_c$  given by this equation and those given by experiment are compared, and on the whole a satisfactory agreement is found except at temperatures under  $10^\circ$ . Of Friedel's methods, the one depending on a vapour density determination seems to give the best results, but it is pointed out that, owing to the very high degree of dissociation of the methylic ether hydrochloride, an exact investigation of the equilibrium is a very difficult task. J. C. P.

**Direct Measurement of the Osmotic Pressures of very dilute Solutions of Sodium Chloride.** By A. PONSOT (*Compt. rend.*, 1899, 128, 1447—1448. Compare this vol., ii, 546).—The osmotic pressures of dilute solutions of sodium chloride (0.110 to 0.115 gram per litre) have been determined by measuring the head of water required to maintain equilibrium between water and the solution with a semi-permeable membrane between. The values obtained for the coefficient  $i$  of Van't Hoff's relation vary from 1.76 to 1.81. From these results and those of Pickering (*Abstr.*, 1892, 1045) on the depression of the freezing point of salt solutions, the author concludes that  $i$  has a limiting value less than, and differing appreciably from, 2. T. H. P.

**Rate of Explosion in Gases.** By DAVID L. CHAPMAN (*Phil. Mag.*, 1899, [v], 47, 90—104).—A mathematical paper in which formulæ are deduced for the maximum rate of explosion and the maximum pressure in the explosive wave. The velocity of explosion is calculated for a number of cases, and the values found are compared with those given by experiment. The formula for the maximum velocity of explosion is also used to calculate some specific heats at constant volume. The data necessary for the calculations have been obtained from Dixon's work on this subject. J. C. P.

**Equilibrium of Three Component Systems forming Two Liquid Phases.** By B. DE BRUYN (*Rec. Trav. Chim.*, 1899, 18, 87; from *Proc. verb. Acad. roy. Sci. Amsterdam*, Jan. 26, 1899).—The equilibrium of the four following systems has been examined: (1) Ammonium sulphate, ethylic alcohol, water; (2) potassium carbonate, methylic alcohol, water; (3) potassium carbonate, ethylic alcohol, water; (4) sodium sulphate, ethylic alcohol, water.

In the first case at a definite temperature, several solutions were obtained homogeneous, but separating into 2 layers when either heated or cooled.

In (3), at  $17^\circ$ , the upper and lower layers contain respectively 91.5 and 0.2 of ethylic alcohol and 0.06 and 52.2 of potassium carbonate per cent., and this composition remains almost constant between  $-18^\circ$  and  $+75^\circ$ . In (2) the upper and lower layers at  $17^\circ$  contain respectively 69.6 and 5.7 of methylic alcohol and 6.25 and 48.4 of potassium

carbonate per cent., and in this case, the temperature exercises a great influence. C. F. B.

**A Method for Carrying Out Chemical Reactions Under High Pressures.** By B. H. HITE (*Amer. Chem. J.*, 1899, 22, 80—86).—The reagents are placed in a platinum tube similar in construction to the ordinary collapsible lead paint-tubes, which is then closed by means of a stopper or screw-cap, and placed in a lead cylinder 5—6 inches long and  $\frac{1}{4}$  inch in diameter; the lead tube is filled with water, and is closed with a lid and placed in a very thick-walled, hollow steel cylinder, into which it accurately fits. The lead tube rests on a steel plug which closes the lower end of the cylinder and rests on the bed-plate of a hydraulic press; the pressure of the ram is communicated to the lid of the lead tube by means of a steel piston, accurately fitting the inside of the hollow cylinder. The platinum tube serves simply to separate the reagents from the water by which the pressure is communicated, and can be replaced by a lead tube if the reagents used are without action on this metal. W. A. D.

**Facilities for Standardising Chemical Apparatus offered by the American and Foreign Governments.** By LOUIS A. FISCHER (*J. Amer. Chem. Soc.*, 1898, 20, 912—927).—An account of methods used in graduating chemical apparatus in the office of Weights and Measures, U.S.A., as compared with those in other countries.

An account, illustrated with photographs of the apparatus, is given of a very quick but accurate method of graduating flasks not too large to be filled with mercury. L. DE K.

**An Electric Drying Oven.** By THEODORE W. RICHARDS (*Amer. Chem. J.*, 1899, 22, 45—49).—The author points out the great advantage of an electric current as a source of heat for drying ovens. An ordinary sixteen-candle incandescent lamp gives heat enough to raise a small oven padded with asbestos to 120° or 130°. He describes a very effective oven which is readily constructed from materials present in every laboratory. The original must be consulted for details. W. A. D.

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### Inorganic Chemistry.

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**Maximum Quantity of Chlorides contained in Sea Air.**  
By ARMAND GAUTIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 391—392).—The chlorine contained in the air at the Rochedouvres lighthouse was determined by aspirating a known volume of the air through a long plug of glass wool, which was afterwards washed with hot water, the filtered washings being titrated with decinormal silver solution. The air was collected during both the day and night, the weather being

fine and dry, and the wind west-north-west, and blowing from the open sea ; the height of the aspirator was 9 metres above sea-level. For a mean temperature of  $15^{\circ}$ , a quantity of chlorine corresponding with 0.022 gram of sodium chloride per cubic metre of air was found. The author regards this as the maximum quantity of salt which air can retain in suspension.

T. H. P.

**Existence of Iodine in the Atmosphere.** By ARMAND GAUTIER (*Bull. Soc. Chim.*, 1899, [iii], 21, 456—463).—Less than 1/500 milligram of free iodine, or gas containing iodine, is present in about 4000 litres of dust-free air of Paris ; similarly, the dust-free air from the sea, forest, or mountain districts contains no appreciable quantity of iodine. No iodine, in the form of soluble salts, is present in the small particles of dust in the air. The air from Paris and from the sea contain respectively 0.0013 milligram and 0.0167 milligram of iodine in 1000 litres. This iodine is probably present in small vegetable organisms suspended in the air. It is detected by filtering the air through glass wool, and afterwards fusing the latter with potash.

R. H. P.

**Action of Iodine on Alkalis.** By E. PÉCHARD (*Compt. rend.*, 1899, 128, 1453—1456).—When iodine is dissolved in sodium hydroxide solution, it exists in three forms, namely, as hypoiodite, iodate, and free iodine, the proportions of these three varying with the conditions. The free iodine diminishes and approaches a limit as the ratio of soda to total iodine increases ; for the ratio  $I:2NaOH$  there is 2 per cent. of free iodine, and this proportion remains appreciably constant as the ratio of soda to iodine is further increased. The amount of hypoiodite formed is approximately proportional to the quantity of soda, and when the mixture has the composition  $I:2NaOH$ , the percentage of iodine in the form of iodate is a maximum, and equal to 92 per cent. of the total iodine. On heating a mixture of the composition  $I+NaOH$  from  $0^{\circ}$  to  $80^{\circ}$ , the amount of free iodine remains sensibly constant, the hypoiodite decreasing and the iodate increasing with rise of temperature. The composition of the mixture gradually changes on standing, the amount of free iodine slowly diminishing and the hypoiodite undergoing conversion very gradually into iodate.

T. H. P.

**Electrolytic Preparation of Fluorine in a Copper Vessel.** By HENRI MOISSAN (*Compt. rend.*, 1899, 128, 1543—1545).—Of all metals, besides platinum, copper is least attacked when in contact with a solution of potassium fluoride in anhydrous hydrogen fluoride undergoing electrolysis. For the preparation of fluorine, the author finds it possible to make the electrolytic vessel of copper, but the electrodes must be of platinum ; the copper probably becomes coated with a layer of insoluble copper fluoride, and, in the case of the electrodes, this coating would diminish the current.

T. H. P.

**Quantity of Oxygen in the Atmosphere, compared with that in the Earth's Crust.** By GERALD STONEY (*Phil. Mag.*, 1899, [v], 47, 565—566).—A calculation is made showing that the quantity of



oxygen in the atmosphere is less than a ten-thousandth part of the combined oxygen in the earth's crust.

J. C. P.

**Some Properties of Liquid Sulphurous Anhydride.** By AUGUST HARPF (*Zeit. angew. Chem.*, 1899, 495—496).—Lange (this vol., ii, 478) has stated that commercial liquid sulphurous anhydride, which may contain as much as 1 per cent. of water, attacks iron at a temperature of 70°, forming a solid crust of ferrous sulphite and thiosulphate; the anhydrous acid does not affect the metal.

The author thinks that at first ferrous sulphite and ferrous hyposulphite are formed; the latter then splits up into water and ferrous thiosulphate.

L. DE K.

**Action of Liquid Sulphurous Anhydride on Iron.** By A. LANGE (*Zeit. angew. Chem.*, 1899, 595—597).—In reply to Harpf (preceding abstract), the author states that he admits the possibility of the presence of hyposulphurous acid in the commercial liquid sulphurous acid, but he has not been able to actually prove its occurrence. The yellow colour of the commercial article is no proof whatever of the presence of hyposulphurous acid, and is often caused by small quantities of lubricating oil.

An analysis is given of a black, crumbly mass formed by corrosion of iron in a refrigerating machine, in which moist sulphurous anhydride was used as cooling agent. Both ferrous sulphite and thiosulphate were detected.

L. DE K.

**The Absorption of Nitrogen.** By WALTHER HEMPEL (*Zeit. anorg. Chem.*, 1899, 21, 19—20).—The best material for the absorption of nitrogen in the preparation of the argon gases is obtained by mixing 1 gram of finely divided magnesium with 5 grams of coarsely powdered calcium oxide and 0.25 gram sodium in pieces of 1—2 mm. diameter.

The volume of nitrogen absorbed in 1 hour by the following materials is, as follows: 1 gram of magnesium 14.5 c.c., 1 gram of lithium 75.5 c.c., 1 gram of magnesium and 5 grams of calcium oxide 122 c.c., 1 gram of magnesium and 3 grams of calcium oxide 50 c.c., 1 gram of magnesium and 8 grams of calcium oxide 31.4 c.c., 5 grams of calcium oxide and 1 gram of sodium 0 c.c., 1 gram of magnesium, 5 grams of calcium oxide and 0.25 gram of sodium 326.2 c.c., 1 gram of magnesium, 5 grams of calcium oxide and 0.11 gram of lithium 228 c.c., and 1 gram of magnesium, 5 grams of calcium oxide and 0.1 gram of sodium 287 c.c.

E. C. R.

**Fluorine Derivatives of Phosphates, Sulphates, Selenates, Tellurates, and Dithionates.** By RUDOLPH F. WEINLAND and J. ALFA (*Zeit. anorg. Chem.*, 1899, 21, 43—69).—Potassium monofluorophosphate (Abstr., 1898, ii, 217) crystallises in the monoclinic system, [ $a : b : c = 0.8501 : 1 : 0.6268$ .  $\beta = 78^\circ 55'$ ].

*Cesium monofluorophosphate*,  $\text{PF}(\text{OH}_3) \cdot \text{OCs}$ , obtained by evaporating a solution of tricesium phosphate (2 mols.) with cesium carbonate (1 mol.) to dryness, and dissolving the residue in excess of hydrofluoric acid, resembles the potassium and rubidium salts in crystalline form and properties. The corresponding sodium, ammonium, and silver salts could not be obtained.

Tripotassium difluorodisulphate (*loc. cit.*) crystallises in the monoclinic system [ $a : b : c = 1.013 : 1 : 0.8218$ .  $\beta = 71^\circ 21'$ ]. *Cæsium difluorodisulphate*,  $\text{S}_2\text{O}_7\text{F}_2\text{Cs}_3\text{H} + \text{H}_2\text{O}$ , is obtained in a similar manner to the potassium salt which it resembles. The corresponding sodium and ammonium salts could not be prepared.

*Tripotassium difluorodiselenate*,  $\text{Se}_2\text{O}_7\text{F}_2\text{K}_3\text{H} + \text{H}_2\text{O}$ , obtained by evaporating a solution of potassium selenate in excess of hydrofluoric acid in a desiccator over lime, crystallises in forms similar to those of potassium fluorosulphate; it quickly decomposes on exposure to the air with loss of water and hydrogen fluoride, and when heated evolves water and hydrogen fluoride, and then oxygen, leaving a residue of selenate and selenium dioxide. The *rubidium* salt,  $\text{Se}_2\text{O}_7\text{F}_2\text{Rb}_3\text{H} + \text{H}_2\text{O}$ , is similar to the potassium salt. The *cæsium* and *sodium* salts could not be obtained. *Ammonium monofluoroselenate*,  $\text{SeO}_3\text{OHFI}(\text{NH}_4)_2$ , obtained on concentrating a solution of ammonium selenate in excess of hydrofluoric acid, crystallises in flat prisms belonging to the rhombic system, quickly loses its lustre on exposure to the air, and dissolves easily in water.

*Potassium difluorotellurate*,  $\text{TeO}_3\text{F}_2\text{K}_2 + 3\text{H}_2\text{O}$ , obtained by evaporating a solution of telluric acid (1 mol.) and potassium hydroxide (2 mols.) to dryness on the water-bath and dissolving the residue in a slight excess of hydrofluoric acid, crystallises in microscopic, octahedral, monoclinic crystals, is fairly stable in dry air, but when heated evolves water and a small quantity of hydrogen fluoride, or at a higher temperature oxygen, and leaves a residue of tellurium dioxide and potassium fluoride. It is difficult to dissolve in water, yielding a faintly acid solution, and cannot be recrystallised from hydrofluoric acid. The *rubidium* salt,  $\text{TeO}_3\text{F}_2\text{Rb}_2 + 3\text{H}_2\text{O}$ , obtained in a similar manner to the potassium salt, crystallises in small, colourless crystals similar to and more easily soluble than those of the potassium salt. The corresponding ammonium and sodium salts could not be prepared.

*Potassium difluorodithionate*,  $\text{S}_2\text{O}_5\text{F}_2\text{K}_2 + 3\text{H}_2\text{O}$ , crystallises from a warm saturated solution of potassium dithionate in hydrofluoric acid, and is extremely unstable. When exposed to the air, it quickly decomposes with evolution of water and hydrofluoric acid, leaving a residue of potassium dithionate; when heated, water and hydrofluoric acid are at first evolved, then sulphurous anhydride, and a residue of potassium sulphate is obtained. The *rubidium* salt is similar in all respects to the potassium salt. *Cæsium monofluorodithionate*,  $\text{S}_2\text{O}_5\text{FIOHCS}_2 + \text{H}_2\text{O}$ , obtained by saturating warm hydrofluoric acid with *cæsium* dithionate, crystallises in small, colourless prisms, and is more stable than the preceding potassium salt, but similar to it in other respects. Sodium and ammonium salts could not be obtained.

E. C. R.

**Decomposition of Carbonic Oxide by Metallic Oxides.** By OCTAVE BOUDOUARD (*Compt. rend.*, 1899, 128, 1522—1523. Compare this vol., ii, 287, 365, and 417).—When carbonic oxide is decomposed at  $800^\circ$  in presence of oxide of nickel or cobalt, or of ferric oxide, the amount of decomposition depends on the time of reaction. The speed of reaction at  $800^\circ$  is greater than at  $650^\circ$ , equilibrium being attained

in 2 hours at the higher temperature, and only after 6 hours at the lower. In the presence of nickel or cobalt oxide at  $800^{\circ}$ , no further change occurs after the gaseous mixture contains 7 per cent. of carbonic anhydride and 93 per cent. of carbonic oxide. T. H. P.

**Decomposition of Carbonic Anhydride in presence of Carbon.** By OCTAVE BOUDOUARD (*Compt. rend.*, 1899, 128, 1524—1525. Compare this vol., ii, 417).—In continuation of the experiments previously described (*loc. cit.*), the reaction between carbonic anhydride and carbon at  $800^{\circ}$  and at  $925^{\circ}$  has been studied. Different forms of carbon were used, namely, wood charcoal, bone black, coke, and carbon reduced from carbonic oxide, the speed of reaction being greatest with the wood charcoal, and least with the bone black. As is the case at  $650^{\circ}$ , so also at  $800^{\circ}$  the decomposition ceases when the composition of the gaseous mixture is the same as that obtained by the action of carbonic oxide on nickel or cobalt oxide at the same temperature—in this case, 7 per cent. of carbonic anhydride and 93 per cent. of carbonic oxide (see preceding abstract). At  $925^{\circ}$ , the proportion of carbonic anhydride in the gaseous mixture is 4 per cent. T. H. P.

**Action of Hydrogen Sulphide on Silicates.** By PAUL DIDIER (*Compt. rend.*, 1899, 128, 1286—1288).—Many natural silicates are partially attacked by hydrogen sulphide at  $1400^{\circ}$ , change colour, and become more soluble in acids, part of the metallic constituents having been converted into sulphides. The quantity which becomes soluble varies with the nature of the mineral from about 7 per cent. (peridot) to 45 per cent. (powdered commercial cerite). In most cases, a small quantity of sulphuric acid is formed, and condenses in the cool part of the tube. The silica displaced by the hydrogen sulphide remains in the free state, usually non-crystalline, or in some cases forms more acidic silicates. Occasionally an annular deposit forms in the cool part of the tube, consisting either of silicon or a silico-formic compound. C. H. B.

**"Condensed" Metallic Hydroxides.** By ERNEST SCHLUMBERGER (*Bull. Soc. Chim.*, 1899, [iii], 21, 467—468).—A claim for priority and a criticism of Wyruboff and Verneuil (this vol., ii, 224). The author prefers the expression "condensation" to that of "polymerisation" used by Wyruboff and Verneuil, since the phenomena observed by them (see this vol., ii, 423) are in the majority of cases accompanied by a loss of water. R. H. P.

**Hydration of Calcium Oxide.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1899, 21, 28—36).—The author has examined qualitatively the hydration of calcium oxide, especially with regard to the influence of a third substance. The hydration is accelerated by the presence of hydrochloric or nitric acid, aluminium, calcium, or barium chloride, acetic acid, sodium acetate, lactic acid, asparagine, or ethylic alcohol. It is retarded by the presence of boric acid, sodium or potassium hydroxide, calcium chromate, potassium dichromate, acetaldehyde, glycerol, cane sugar, or dextrose. The following compounds do not influence the hydration: ammonia, calcium hydroxide,

sodium and lithium chlorides, potassium hydrogen carbonate, and potassium nitrate. E. C. R.

**Mixed Halogen Lead Salts.** By VICTOR THOMAS (*Compt. rend.*, 1899, 128, 1329—1331).—When lead iodide is dissolved in a hot saturated solution of lead bromide and the liquid is allowed to cool, lead iodide is first deposited, then greenish-yellow needles of the compound  $PbI_2 \cdot 3PbBr_2$ , and finally lead bromide. If the first precipitate of lead iodide is not removed, it is gradually converted, as the liquid cools, into the bromiodide. When the double salt is heated with water, it decomposes and dissolves, but is formed again when the liquid cools. Similar phenomena are observed with a solution of the iodide in the chloride. The formation and decomposition of these salts at different temperatures is in accordance with Van't Hoff's law connecting with the heat of formation of the compounds, the changes in composition produced by changes in temperature. Since the simple and double salts can crystallise together, it follows that the composition of the crystals will oscillate between two limits, but they are not to be regarded as mere mixtures of isomorphous compounds (compare Abstr., 1898, ii, 585, and this vol., ii, 420). C. H. B.

**Copper Reduced at a Low Temperature.** By ALBERT COLSON (*Compt. rend.*, 1899, 128, 1458—1460).—On reducing cupric oxide at temperatures near  $200^\circ$  by means of hydrogen or carbonic oxide, an active form of the metal termed nascent copper is obtained. In contact with bromine, it takes fire, even after being cooled to  $-21^\circ$ , or after placing in a vacuum; in moist air, however, it loses this property. With nitric acid, it does not form nitric oxide, but is more rapidly attacked than ordinary copper filings. In density, magnetic properties, and action on a nitric acid solution of a ferric salt, it shows no difference from copper reduced at a red heat. On hammering, "nascent" copper loses its active properties. T. H. P.

**Vapours Emitted by the two Varieties of Mercuric Iodide.** By DESIRÉ GERNEZ (*Compt. rend.*, 1899, 128, 1516—1519).—The vaporisation of mercuric iodide was observed in a special vacuum apparatus in which the temperatures of both the vaporising and the condensing surfaces could be varied. The vapour given off at all temperatures by the yellow crystals deposits yellow, orthorhombic crystals, no matter what may be the temperature of the cooler surface on which deposition occurs. The yellow crystals are also obtained from the vapour emitted when the red variety is vaporised at any temperature from  $25^\circ$  up to the point at which the change into the yellow form takes place. If, however, the cool surface is lightly rubbed with the red crystals, the form deposited is also red. T. H. P.

**Action of Water on Ammonium and Potassium Mercuriodides.** By MAURICE FRANÇOIS (*Compt. rend.*, 1899, 128, 1456—1458).—Ammonium mercuriodide,  $HgI_2 \cdot NH_4I + H_2O$ , is decomposed by water, mercuric iodide being precipitated; at ordinary temperatures, the solution formed contains approximately one molecule of  $HgI_2$  to two of  $NH_4I$ . To determine whether the compound  $HgI_2 \cdot 2NH_4I$  exists in the solution, the action of water on the double iodide has

been studied at three different temperatures, and it is found that, at  $55^\circ$ , about half the mercuric iodide of the salt is precipitated, whilst at  $20^\circ$  and  $90^\circ$  the quantities of mercuric iodide thrown down are respectively much less than and much greater than the half of that contained in the double iodide. Similar behaviour is shown by potassium mercuriodide,  $\text{HgI}_2 \cdot \text{KI} + 5\text{H}_2\text{O}$ , so that when water acts on these compounds, the solution contains no definite salt, but is merely a solution of mercuric iodide in the alkali iodide solution.

T. H. P.

**Constitution of the Oxides of the Rare Metals.** By GREGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Compt. rend.*, 1899, 128, 1573—1575. Compare this vol., ii, 224 and 423).—Several hydrated salts of cerium contain water of crystallisation in such proportion that the number of molecules is only integral when multiplied by 3, and in certain double salts 3 mols. of cerous oxide are combined with 1 mol. of a salt of a monad metal; these facts have been advanced as an argument in favour of the trivalency of cerium. The authors call attention to the invalidity of such an argument, which entirely disregards the existence of such compounds as  $(\text{CdSO}_4)_3 + 8\text{H}_2\text{O}$ , exactly analogous to  $(\text{CeSO}_4)_3 + 8\text{H}_2\text{O}$ ;  $5\text{HgCl}_2$ ,  $\text{RbCl}$ ; and  $\text{ThSO}_4$ ,  $\text{K}_2\text{SO}_4$ , the formation of which would thus disagree with the supposed quadrivalency of thorium.

On evaporating at  $60$ — $70^\circ$  a solution of cerium, lanthanum, didymium, or yttrium sulphate in concentrated nitric acid, well-crystallised compounds of the general formula  $2(\text{MSO}_4) \cdot \text{M}(\text{NO}_3)_2 + n\text{H}_2\text{O}$  are obtained,  $n$  being equal to 2 for the cerium and lanthanum compounds, and 6 for those of didymium and yttrium. The substances are very stable, and can be recrystallised from concentrated nitric acid without undergoing change. Further, Job (*Abstr.*, 1898, i, 356) has prepared stable compounds of the composition  $2\text{MC}_2\text{O}_4 \cdot \text{MCl}_2 + 6\text{H}_2\text{O}$ . The formulæ of these two series of substances show that the oxides exist in the oxalates and sulphates in a triple form, one of the MO groups having chemical functions different from those of the other two.

T. H. P.

**Lanthanum Peroxide.** By PETR G. MELIKOFF and L. PISSARJEWSKY (*Zeit. anorg. Chem.*, 1899, 21, 70—72).—*Lanthanum peroxide* is obtained by dissolving pure lanthanum oxide in nitric acid, and after adding hydrogen peroxide, precipitating with potassium hydroxide. The white, gelatinous precipitate, which is similar in appearance to aluminium hydroxide, is washed with hydrogen peroxide, then with water, and dried on a porous plate. The determination of the ratio of active oxygen to  $\text{La}_2\text{O}_3$  gave  $20:\text{La}_2\text{O}_3$ , so that the formula is  $\text{La}_2\text{O}_5 + n\text{H}_2\text{O}$  or  $\text{HLaO}_3 + n\text{H}_2\text{O}$ . When treated with dilute sulphuric acid, it yields hydrogen peroxide, with concentrated acid, ozonised oxygen, and with carbonic anhydride, hydrogen peroxide and lanthanum carbonate; when left in a desiccator over sulphuric acid and soda lime, it gradually decomposes with loss of oxygen, but is not completely decomposed even by prolonged heating at  $200^\circ$ . Lanthanum peroxide, like the oxide, has basic properties, and does not combine with bases to form salts.

E. C. R.

**Ferric "Hydrogel."** By JACOBUS M. VAN BEMMELN (*Rec. Trav. Chim.*, 1899, 18, 86; from *Proc.-verb. Acad. roy. Sci. Amsterdam*, Jan. 26, 1899. Compare Abstr., 1893, ii, 169).—A study of the isotherm, for 15°, of dehydration, rehydration, and re-dehydration of gelatinous ferric hydroxide shows that the composition of this substance varies with the amount of moisture in the air; no definite hydrate exists, contrary to Spring's conclusion (Abstr., 1898, ii, 520), and the substance is merely  $\text{Fe}_2\text{O}_3$  containing absorbed water. C. F. B.

**Chromic Chloride.** By PAUL ROHLAND (*Zeit. anorg. Chem.*, 1899, 21, 37—42).—The violet chromic chloride is almost insoluble in boiling water, but if 1/20,000 part of chromous chloride is present, it is easily dissolved, being converted into the green chloride, and the solution, on cooling, deposits hygroscopic needles of the composition  $\text{CrCl}_3 + 6\text{H}_2\text{O}$ . The author explains the conversion on the dissociation theory, and finds that it is retarded by ethylic or methylic alcohol or acetone. E. C. R.

**Uranium Compounds.** By JULES ALOY (*Bull. Soc. Chim.*, 1899, [iii], 21, 613—616).—In contact with hot potassium or sodium hydroxide solution, crystallised uranous sulphate is rapidly converted into a black, crystalline product, the liquid remaining colourless. This product, which is readily freed from acid and alkali by washing with hot water, has the composition  $\text{UO}_2 + 2\text{H}_2\text{O}$ , and remains unchanged in the air for several days; on heating, it is completely transformed into the green oxide, and as it is soluble in dilute acids, it affords a ready means of preparing uranous salts.

Uranous chloride is formed when a hydrochloric acid solution of uranic hydroxide, or of the green oxide, is exposed, in presence of a small quantity of alcohol, to the action of sunlight. From the solution thus prepared, it can be obtained in pale green crystals by the addition of ether.

Berzelius found that, on heating a solution of uranous chloride for some hours, a black precipitate was produced; the author finds this to be an oxychloride of the composition  $\text{UCl}_4 \cdot 5\text{UO}_2 + 10\text{H}_2\text{O}$ . It can be kept in the air for a long time without turning yellow, and on drying over sulphuric acid presents a shining conchoidal fracture; washing with water removes some of the chlorine.

Uranous oxalate can be obtained crystalline (1) by leaving uranous hydroxide in contact with oxalic acid solution, or (2) by adding oxalic acid solution to a sulphuric acid solution of uranous hydroxide; it forms faintly greenish-white, elongated rectangular prisms of the composition  $\text{U}(\text{C}_2\text{O}_4)_2 + 6\text{H}_2\text{O}$ , and is insoluble in water. Potassium or sodium hydroxide solution decomposes it, giving a voluminous precipitate of uranous hydroxide, and on heating in a current of hydrogen, it is converted into dioxide.

On mixing recently precipitated uranous hydroxide with a cold dilute solution of arsenic acid, uranous arsenate,  $\text{UH}_2(\text{AsO}_4)_2 + 2\text{H}_2\text{O}$ , gradually separates in thin, pale green needles, stable at ordinary temperatures; it is insoluble in water, but dissolves partially in excess of arsenic acid. T. H. P

## Mineralogical Chemistry.

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**Indium in Tungsten Minerals.** By ELIZABETH A. ATKINSON (*J. Amer. Chem. Soc.*, 1898, 20, 811—813).—The author confirms Hoppe-Seyler's observation as to the presence of indium in wolframite from Zinnwald, and in support of his suggestion that the indium was really present in the zinc blende accompanying this mineral, shows that neither indium nor zinc was present in other tungsten minerals, namely, wolframite from Cornwall, hübnerite from Colorado, and scheelites from New Zealand and Bohemia.

L. DE K.

**Phosphorus and Arsenic in Minerals of the Island of Elba.** By P. TOSO (*Zeit. Kryst. Min.*, 1899, 31, 406; from *Boll. R. Com. Geol.*, 1897, 28, 216—248).—Thirteen analyses by Mattiolo and Aichino of iron ores from Elba show the presence of Fe, 59·38—67·26; P, trace to 0·785; As, trace to 0·315 per cent.

L. J. S.

**Iodine and Bromine in Fumarole Products from Vesuvius.** By R. VITTORIO MATTEUCCI (*Zeit. Kryst. Min.*, 1899, 31, 399; from *Rend. Accad. Sci. Fisiche, etc., Napoli*, 1897, [iii], 3, 151—152).—Iodine and bromine have been detected in the fumarole products of the Vesuvian eruption of 1895.

L. J. S.

**Selenium in Fumarole Products from Vesuvius.** By R. VITTORIO MATTEUCCI and ERCOLE GIUSTINIANI (*Zeit. Kryst. Min.*, 1899, 31, 399; from *Rend. Accad. Sci. Fisiche, etc., Napoli*, 1897, [iii], 3, 100—101).—A bright red incrustation, formed during the eruption of July 3, 1895, was found to contain selenium, together with fluorine, phosphorus, and boron.

L. J. S.

**Saline Sublimation from Vesuvius.** By PASQUALE FRANCO (*Zeit. Kryst. Min.*, 1899, 31, 399; from *Rend. Accad. Sci. Fisiche, etc., Napoli*, 1897, [iii], 3, 192—196).—A greenish or white granular sublimation product of the last Vesuvian eruption has the following composition:

NaCl.	KCl.	K <sub>2</sub> SO <sub>4</sub> .	CuCl <sub>2</sub> +2H <sub>2</sub> O.	Fe <sub>2</sub> Cl <sub>6</sub> +6H <sub>2</sub> O.	PbCl <sub>2</sub> .	CaCl <sub>2</sub> .	Total.
77·08	8·44	8·44	3·21	1·61	0·24	0·98	100·00

Also traces of MgCl<sub>2</sub>, NH<sub>4</sub>Cl, ZnCl<sub>2</sub>, and TiCl<sub>2</sub>, but no helium.

L. J. S.

**Sodium Hydrogen Carbonate on Vesuvian Lava.** By R. VITTORIO MATTEUCCI (*Zeit. Kryst. Min.*, 1899, 31, 400; from *Rend. Accad. Sci. Fisiche, etc., Napoli*, 1897, [iii], 3, 223—232).—The presence of sodium hydrogen carbonate, together with sodium carbonate, sulphate, and chloride, is noted in a saline incrustation on Vesuvian lava of 1895.

L. J. S.

**Composition of Parisite from Montana.** By SAMUEL L. PENFIELD and CHARLES H. WARREN (*Amer. J. Sci.*, 1899, [iv], 8, 21—24).—The rare mineral parisite has recently been found in Montana in a

white, loosely coherent matrix, having the appearance of a decomposed rhyolite. The specimens are supposed to have come from near Pyrites, Ravalli Co. The yellowish-brown crystals average 1 mm. in diameter and 1 cm. in length, and are scattered with crystals of pyrites throughout the white matrix. They are hexagonal, and show oscillations between prisms and steep pyramids; goniometric measurements are given. Analysis of impure material gave I. Analysis II is of a pure crystal from Muso, Colombia, S.A., the original locality for parasite (analyses I and II by Warren).

										Total less O
CO <sub>2</sub> .	F.	Ca <sub>2</sub> O <sub>3</sub> .	(La, Di) <sub>2</sub> O <sub>3</sub> .	CaO.	Fe <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Gangue.	for F. Sp. gr.
I. 22·93	5·90	26·14	28·46	10·98	0·80	0·69	0·19	0·26	[6·13]	100·00 4·128
II. 24·22	6·82	30·67	29·74	10·70	0·20	0·20	0·10	—	—	99·78 4·302

The second analysis gives the formula  $2(R'''F)CO_3 + CaCO_3$  or  $(R'''F)_2Ca(CO_3)_3$ . L. J. S.

**Formula of Tourmaline.** By H. RHEINECK (*Zeit. Kryst. Min.*, 1899, 31, 385—386).—The formula for tourmaline recently proposed by Penfield and Foote is  $H_{20}B_2Si_4O_{21}$  (this vol., ii, 334). If, however, the fluorine in their analyses is combined with the metals, the ratio of Si : H is 4 : 19·33. This taken with the extreme ratios, Al : Si = 1 : 0·75 and 1 : 1·21, pointed out by Rheineck in 1893, gives the two general formulæ,  $H_5Al_8B_3Si_6O_{31}$  and  $H_{14}Al_5B_3Si_6O_{31}$ , with the intermediate members  $H_8Al_7B_3Si_6O_{31}$  and  $H_{11}Al_6B_3Si_6O_{31}$ . Such acids with  $B_3Si_6$  could contain 27, 29, 31, or 33 hydroxyl groups, and this agrees with the results of Riggs' (1888) analyses. L. J. S.

**Origin of Glaucophane Rocks.** By HARRY ROSENBUSCH (*Chem. Centr.*, 1899, i, 451; from *Sitz.-ber. Akad. Berlin*, 1899, 706—717).—The arfvedsonite-amphiboles (arfvedsonite, riebeckite, hastingsite, &c.) occur only as original constituents of eruptive rocks, whilst the "glaucamphiboles" or glaucophane-amphiboles (glaucophane, gastaldite, crossite) occur only in dynamo-metamorphic rocks. The chemical composition (as shown by two quoted analyses) of glaucophane-rocks is identical with that of a normal gabbro magma, and there is also microscopic evidence to show that glaucophane-rocks owe their origin to the dynamo-metamorphism of gabbros, diabases, &c. In these rocks, the alkali is present in the glaucophane, whilst in orthoamphibolites, which may also be derived from gabbros, &c., the alkali is present in feldspar. L. J. S.

**Eruptive Rocks of Cape Blanc in Algeria.** By LOUIS DUPARC and E. RITTER (*Compt. rend.*, 1899, 128, 1356—1358).—The eruptive rocks of Cape Blanc in Algeria contain biotite, with inclusions of apatite or more rarely of zircon; hornblende (also with inclusions of apatite) usually much altered in appearance, and small in quantity; plagioclases, chiefly of a somewhat basic type. There is no regular succession of the felspathic zones. Quartz is rarely present and is much altered. The second consolidation is sometimes a colourless isotropic glass, with perlitic fissures, but in most cases the matrix is crystalline and of a distinctly microgranulitic structure. Quartz is abundant and encloses chloritic biotite and opaque grains of an iron



compound. The microgranulitic matter contains  $\text{SiO}_2$ , 63.0 to 67.88;  $\text{Al}_2\text{O}_3$ , 14.45 to 17.40;  $\text{Fe}_2\text{O}_3$ , 5.03 to 5.74;  $\text{CaO}$ , 5.19 to 5.71;  $\text{MgO}$  and alkalis, 6.27 to 8.38; loss on heating, 0.47—0.48. The rocks are neovolcanic quartz-porphyrries of a basic character with microgranulitic or vitrophyric structure.

C. H. B.

**Iodine in the Mineral Waters of Royat.** By ANDRÉ DUBOIN (*Compt. rend.*, 1899, 128, 1469—1470).—The author has tested water from the Eugénie spring at Royat for the presence of iodine. Potassium hydroxide solution was added until alkaline to prevent the formation of calcium or magnesium iodide and the estimation then carried out by Gautier's method (this vol., ii, 477); by this means, no iodine was detected. On evaporating the water to dryness and fusing the residue with caustic potash, 0.04 milligram of iodine per litre was found. The author is therefore of opinion that the iodine is present in organic combination; this would explain the fact that the waters lose some of their characteristic properties on keeping. T. H. P.

**Fluorine in Mineral Waters.** By CHARLES LEPIERRE (*Compt. rend.*, 1899, 128, 1289—1291).—The author maintains that, contrary to the view of Parmentier (this vol., ii, 501), small quantities of fluorine are not uncommon in mineral waters, their presence having been observed by many chemists. The mineral water of Gerez, in the north of Portugal, is exceptional; it contains only 0.296 to 0.310 gram of solid matter per litre, but of this 0.022 to 0.025 gram is an alkali fluoride, probably sodium fluoride. The presence of this unusual constituent may be an important factor in the well-known therapeutic value of this water in liver complaints.

For the detection of fluorides in natural water, the formation of microscopic crystals of sodium silicofluoride with their well-defined form is frequently of value.

C. H. B.

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## Physiological Chemistry.

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**Influence of Alcohol on Respiration in Man.** By HERMANN WENDELSTADT (*Pflüger's Archiv.*, 1899, **76**, 223—275).—Large doses of alcohol increase the respiration in most cases in men who are not fatigued, although sometimes only to a small extent. In fatigued individuals, the increase is always seen, and is much greater. This action is seen at its best if the alcohol is administered as a wine with rich bouquet.  
W. D. H.

**Modifications in Metabolism produced by Diphtheria Toxin.** By DIARMID NOËL-PATON, JAMES CRAUFURD DUNLOP, and IVISON MACADAM (*J. Physiol.*, 1899, **24**, 331—355).—Under the influence of the diphtheria toxin in the dog, the digestion and absorption of proteids are not interfered with, but there is a great increase in proteid katabolism; the amounts of urea, ammonia, and uric acid are not

affected, but the increase of urinary nitrogen is in some other form. Similarly, the sulphur, but not the sulphuric acid, is increased in the urine. The phosphorus of the urine is not increased, so apparently there is no increase in the katabolism of nucleins. There is no marked alteration in the proportion of sodium and potassium, but the excretion of chlorine is markedly lessened. W. D. H.

**Action of Various Substances on the Activity of Saliva.** By F. KÜBEL (*Pflüger's Archiv.*, 1899, 76, 276—305).—With regard to sodium chloride, the more concentrated the starch, the more concentrated must a salt solution be to exercise an inhibitory influence on saliva; or, to put it another way, a salt solution of such a strength that it delays the salivary digestion of starch of a certain degree of concentration will further its activity when the starch is more concentrated. Using dilute solutions of corresponding strengths, salivary digestion is furthered by sodium fluoride, then follow in the order named the chloride, bromide, and iodide, the last having the least action; as the saline solutions increase in strength, the action becomes less and less, and finally the activity of saliva is hindered. The corresponding potassium salts act similarly, but less energetically, than those of sodium. Alkali diminishes, but very dilute acid favours, salivary action. W. D. H.

**Relative Volume or Weight of Blood-corpuscles and Plasma.** By GEORGE N. STEWART (*J. Physiol.*, 1899, 24, 356—373).—The relative quantity of corpuscles and serum in defibrinated blood can be determined by adding to a definite quantity of the blood a known amount of a solution of hæmoglobin in the serum of the blood, centrifugating, and comparing the concentration of the hæmoglobin in the serum and in the original solution. The relation can also be determined by measuring the electrical conductivity of the blood and serum, and substituting the values in the formula  $p = \lambda_{(b)} / \lambda_s (180 - \lambda_{(b)} - \sqrt{\lambda_{(b)}})$ , or in the formula  $p = 174\lambda_{(b)} - (\lambda_{(b)})^2 / \lambda(s)$ , where  $\lambda_{(b)}$  is the conductivity of the blood at  $5^\circ \times 10^8$ ,  $\lambda(s)$  that of the serum, and  $p$  the number of c.c. of serum in 100 c.c. of blood. In the dog,  $p$  varies from 40 to 74. W. D. H.

**Influence of Carbonic Anhydride and of Alkali respectively on the Anti-bacterial Properties of Blood and Similar Fluids.** By HARTOG J. HAMBURGER (*Virchow's Archiv.*, 1899, 156, 329—374).—If carbonic anhydride is allowed to act on blood, the bactericidal powers of the serum are increased; this is due to (1) the greater concentration of the serum, for, under the influence of the gas, the red corpuscles take up water; (2) the anti-bacterial power of the carbonic anhydride itself, and (3) the increase in the serum of diffusible alkali; this comes partly from the corpuscles, partly from the albuminates of the serum. For similar reasons, the serum of normal venous blood is more bactericidal than that from arterial blood. The blood from positions of venous congestion, œdema fluid, and exudations containing numerous cells (like 'laudable pus'), possess increased anti-bacterial power. W. D. H.

**Physiological Relationships of Lactose, especially on the Intestine.** By ERNST WEINLAND (*Zeit. Biol.*, 1899, 38, 16—62).—In sucking animals (including the new-born child), there is in the small intestine a ferment, *lactase*, which is soluble in water, and capable of hydrolysing milk sugar. This is present also in the full-grown dog, pig, and horse, but not in the full-grown ox, sheep, rabbit, and hen. In the case of the calf, 22—23 grams of lactose were inverted in a digestion lasting  $4\frac{3}{4}$  hours at  $39^{\circ}$ . After several months feeding on milk, the rabbit, and even the hen, develop the ferment in their intestine. In the dog, feeding on milk sugar does not increase the glycogen in the liver; a rise of the respiratory quotient is attributed to the bacterial decomposition of the sugar in the intestine.

W. D. H.

**Influence of Inanition on the Glycogen in the Animal Body.** By EDUARD PFLÜGER (*Pflüger's Archiv.*, 1899, 76, 1—20).—The author's present experiments on hens, together with those of others quoted, show that the glycogen in the liver and in the muscles steadily sinks as inanition progresses. This is entirely at variance with C. Voit's idea that glycogen can increase from the splitting up of fat or proteid during the winter sleep of hibernating animals.

W. D. H.

**Conversion of Nuclein Bases into Uric Acid by the Action of Oxygen on Tissue Extracts.** By WILHELM SPITZER (*Pflüger's Archiv.*, 1899, 76, 192—203).—By the digestion of extracts of liver and spleen at  $40^{\circ}$ , air being allowed to bubble through them and putrefaction being excluded, uric acid is formed; this is due to the oxidation of xanthine, hypoxanthine, and, to a less extent, of adenine and guanine. This confirms Horbaczewski's previous work.

W. D. H.

**Chemical Stimulation of Nerve-containing and Nerve-less (Curarised) Skeletal Muscles.** By G. ZENNECK (*Pflüger's Archiv.*, 1899, 76, 21—58).—Curarised muscles in the frog contract more strongly to chemical stimuli (ammonia, ether, chloroform) than muscles which contain nerves. Solutions which stimulate motor nerves work more vigorously on nerveless muscles. Attention is directed at some length to the graphic record of such contractions.

W. D. H.

**Physiological Effects of Peptone.** By WILLIAM H. THOMPSON (*J. Physiol.*, 1899, 24, 374—409. Compare Abstr., 1897, ii, 60).—Amphopeptone retards, antipeptone hastens, coagulation; with proteoses, both phases are obtained. All the ingredients of Witte's peptone, except antipeptone, possess vaso-dilating powers; the increasing order of potency is amphopeptone, deuteroproteose, heteroproteose, and protoproteose; this is due to a direct effect on the walls of the vessels. Tracings are given which show this effect on the intestinal, and to a less extent on the renal vessels.

W. D. H.

[Physiological Action of] Aspirin (Acetylsalicylic Acid). By HEINRICH DRESER (*Pflüger's Archiv.*, 1899, 76, 306—318).—It is essential that, if salicylic preparations are to be of any medicinal value, they must be in such a form that salicylic acid is liberated as soon as possible after absorption. The unpleasant taste of sodium salicylate has led to the introduction of numerous salicyl compounds, in many of which an alkyl group has been introduced. The present paper suggests an acetyl group is better, and specially praises acetylsalicylic acid, for which the name *aspirin* is suggested. It is easily split up by the gastric juice, or after absorption in the alkaline fluids of the body; its action on the nervous system is not so irregular as that of sodium salicylate, and, moreover, it stimulates the heart instead of depressing it as the sodium salt does. W. D. H.

Physiological and Toxicological Study of Ivy and Hederin. By ALBERT JOANIN (*Compt. rend.*, 1899, 128, 1476—1478).—On cold-blooded animals, hederin has not a very strong toxic action, 5 milligrams being required to kill a frog of from 35 to 40 grams weight; a slow and progressive paralysis sets in, death occurring after 24 or 30 hours. With warm-blooded animals, the action is more intense, the doses necessary to produce death being 5 to 7, 3 to 4, or 2 to 3 centigrams per kilogram of body weight, according as the injection is hypodermic, intraperitoneal, or intravenous. In all three cases, the symptoms are prostration, shivering, hypothermy often very accentuated, flatulence, diarrhoea sometimes sanguineous, coma, and death. When injected into a dog's stomach, hederin causes abundant vomitings and has also a very pronounced purgative action. Hederin causes a lowering of the arterial pressure which is transitory for small doses, but with large doses the decrease of pressure increases until death occurs. Hederin is hence an emeto-cathartic, and to its presence ivy owes its emetic and purgative effects; the nervous symptoms caused by ivy are probably due to some other principle. T. H. P.

Toxic Action of Sodium Fluoride. By HERBERT B. BALDWIN (*J. Amer. Chem. Soc.*, 1899, 21, 517—522).—Sodium fluoride, taken in doses varying from about 0.25 to 9 grams, produces nausea, vomiting, and salivation, also frequently diarrhoea, the effects varying in intensity, of course, with the constitution of the individual. In one case, where a man accidentally took at least 10 grams, death ensued within 24 hours. In cases of suspected poisoning, the urine may be advantageously tested for fluorine. Sodium fluoride ought to be included as a second-class poison in works on toxicology.

L. DE K.

## Chemistry of Vegetable Physiology and Agriculture.

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**Alcoholic Fermentation without Yeast Cells. IX.** By EDUARD BUCHNER and RUDOLF RAPP (*Ber.*, 1899, 32, 2086—2094. Compare this vol., ii, 236).—As the result of numerous experiments, the following conclusions are drawn:

1. When yeast which has been well triturated with kieselg  hr and quartz sand is fractionally filtered under a pressure of 60 kilos. per square cm., the liquid which runs through first is far less active than the later fractions, the most active portion being obtained by a second trituration and filtration without the addition of more water. From 1200 grams of yeast, with the gradual addition of 65 c.c. of water, 730 c.c. of active extract may be obtained. When, however, the extract is filtered through biscuit porcelain, the first 20 c.c. are much more active than any of the subsequent fractions.

2. Fermentation takes place equally readily with solutions of sugar containing from 15 up to 30 per cent. of sugar; in each case, toluene is added, and the temperature kept at 23°. When sugar is not present, very little fermentation takes place, the maximum amount of carbonic anhydride evolved from 20 c.c. of extract being after 40 hours 0.06 gram, and after 88 hours 0.1 gram.

3. Starch itself is not fermented by the extract, but "soluble starch" and dextrans of various origins are readily fermented (compare *Abstr.*, 1898, i, 396).

4. Glucose and fructose are fermented at practically the same rate as one another, both by yeast extract and by fresh Munich bottom yeast. This conclusion, however, is not in accord with statements made by other authorities (compare Duclaux, Prior, and Kayser).

5. The previous irregularities (*Abstr.*, 1898, i, 396 and 480) noticed on the addition of potassium arsenite to the yeast extract, are probably to be explained by the proteids in the extract protecting the zymase from the action of the arsenite, as it has been found that the dilution of the extract with water, in the presence of 2 per cent. of arsenite, practically stops fermentation, whereas dilution with blood serum or liquids rich in proteids, or even sugar solution, in the presence of the same amount of arsenite, retards the fermentation to a slight extent only. Glucose can also be fermented to a certain extent by yeast extract in the presence of arsenite.

J. J. S.

**Formation of Glycogen in Yeast Extract.** By MAX CREMER (*Ber.*, 1899, 32, 2062—2064).—The extract obtained from fresh yeast gives the usual glycogen reactions, but these are no longer shown when the extract has been kept for some 6—12 hours. If, however, those extracts which give little or no glycogen reaction are mixed with 10 per cent. or stronger solutions of fermentable sugars and then investigated at the end of 12—24 hours, it is found that, in most cases, the presence of glycogen can be again detected. Fresh yeast and a temperature of 10—12° appear to be the necessary factors. The newly-formed glycogen exhibits less opalescence than that originally

present. The bearing of this discovery on the theory of the reactions in yeast extract is given. J. J. S.

**Decomposition of Cement under the Influence of Bacteria.** By GEORG BARTH (*Zeit. angew. Chem.*, 1899, 489).—In reference to Stutzer and Hartleb's work on this subject (this vol., ii, 505), it is stated that the decomposition of cement may take place in a comparatively short time. In one particular case, the cement crumbled after the water reservoir had been in use for only three years. The following analyses show that a large proportion of the lime had been washed out :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.
Original Portland cement...	20·0	7·5	3·5	63·0	2·0
Disintegrated cement .....	33·21	21·84	10·94	24·23	9·36

L. DE K.

**Physiological Significance of Alcohol in the Vegetable Kingdom.** By P. MAZÉ (*Compt. rend.*, 1899, 128, 1608—1610).—When peas are placed in contact with water, they gradually diminish in weight and in the water relatively large quantities of alcohol are found. Thus 100 peas in 100 c.c. of water at 22—23° yielded 4·63 per cent. of their weight of alcohol in 4 days and 10·54 per cent. in 13 days ; starch and small quantities of reducing sugars were also found in the water. Peas from which the embryos have been removed give a similar production of alcohol and also a distinct odour of aldehydes. Alcohol thus appears to be a normal and necessary product of the digestion of the carbohydrates of peas during development and it is probably formed at the expense of the glucoses in the living cells by a diastatic process. T. H. P.

**Lability and Energy in Relation to Protoplasm.** By OSCAR LOEW (*Imp. Univ. Coll. of Agric. Tokyo, Bul.*, 1897, 2, 393—405. Compare "The Energy of Living Protoplasm," London, 1896).—Albumin is produced by the condensation of the hypothetical aspartaldehyde which is formed in plant cells either from asparagine or from formaldehyde and ammonia. The albumin of living protoplasm differs chemically from that of dead protoplasm. Plants frequently contain, as reserve material, a highly labile aldehydic form of albumin. The chemical nature of this substance is altered by the same influences as those by which the protoplasm is killed. It is believed that active albumin gives rise to living matter.

The lability of the albumin of living protoplasm is due to the presence of aldehyde and amido-groups.

The conversion of the albumin of living into that of dead protoplasm presents a remarkable analogy to the transformation of an unstable substance into a stable modification. N. H. J. M.

**The Causes of the Transformation of Sap-wood into Wood in Oaks (*Quercus Robur* and *Q. Pedunculata*).** By ÉMILE MER (*Ann. Agron.*, 1899, 25, 281—289).—During the change of sap-wood into wood, the reserve of starch is partly resorbed and an abundant production of tannin takes place. The latter, being unable to spread

to any extent in the duramen already formed, remains in the radial and woody cells.

When dead wood is in contact with live wood, there is, as a rule, a migration of tannin, and, in the case of conifers, of resin from the latter; starch, however, does not penetrate into the dying wood. The migration of tannin is due to evaporation in the dead wood.

The following observations were made after a ring of bark was removed from the trunk of an oak. At first there was an accumulation of starch; subsequently, as the outside decayed, the amount of tannin increased.

The tannin in fully-developed wood is produced from the starch present in the same layer, from a part of the starch present in the younger woody rings, and from the starch which is resorbed in the sap-wood.

N. H. J. M.

**Commercial Varieties of Maté.** By EDUARD POLENSKE and WALTER BUSSE (*Chem. Centr.*, 1899, i, 442; from *Arb. Kais. Ges.-A.*, 15, 171—177).—Four samples of maté from Brazil were examined: (1) finely-divided side-portions, mostly young leaves; (2) coarsely-ground sample, containing old leaves; (3) the same with numerous mid-ribs and stalks; (4) a sample containing 50 per cent. of very roughly-ground stems and stalks. The percentage composition is as follows:

	Water.	Extract.	Tannin.	Soluble or- ganic matter (excl. tannin).	Caffein.	Ash.	In ash. Mn <sub>3</sub> O <sub>4</sub> . Fe <sub>2</sub> O <sub>3</sub> &Al <sub>2</sub> O <sub>3</sub> .	
1.	6.79	36.66	9.59	22.25	0.88	6.00	5.51	4.03
2.	6.78	35.63	8.87	22.17	0.71	6.02	6.45	4.21
3.	6.98	34.13	8.10	21.83	0.53	5.44	5.90	3.00
4.	7.26	30.56	6.68	19.93	0.50	5.66	4.51	3.47

N. H. J. M.

**Oil of Maize.** By CYRIL G. HOPKINS (*J. Amer. Chem. Soc.*, 1898, 20, 948—961).—This fat, which belongs to the drying oils, has the following composition: Cholesterol, 1.37; lecithin, 1.49; stearin (?), 3.66; olein, 44.85; linolein, 48.19; total, 99.56 per cent. It has a sp. gr. varying from 0.9245 to 0.9258, and solidifies at about -36°. When the temperature is gradually raised, it becomes transparent at -14°, but does not actually fuse below -2.4°.

L. DE K.

**Employment of Mangel Wurzels in Cattle Feeding.** By L. BRÉTIGNIÈRE and DUPONT (*Ann. Agron.*, 1899, 25, 257—281).—Sheep-feeding experiments were made with three varieties of mangolds, (1) tankard, (2) a rich variety, and (3) an intermediate variety, the average weight (in grams) and the composition of which was as follows:

	Dry		Sugar.	Per cent. in dry matter.				Ether extract.	Ash.
	Av. wt.	matter.		Organic N.	Nitric N.	Cellulose.			
1.	1446	15.7	56.0	1.63	0.157	4.5		0.08	6.54
2.	454	22.3	70.1	1.10	0.030	5.2		0.3	4.0
3.	614	18.0	62.7	1.39	0.138	4.3		0.3	5.26

The juice contained (1) 9.4, (2) 16.6, (3) 12.1 per cent. of sugar, and the sugar in the roots amounted to (1) 8.8, (2) 15.6, and (3) 11.3 per



cent. The yield of roots was 45830, 37000, and 44660 kilograms per hectare. The amounts of roots given in the daily rations were in proportion to the yield per hectare, being obtained in each case from an equal area of ground.

The results showed that the third variety (intermediate) gave the greatest increase in live weight, and the tankard much the least. The better results obtained with the intermediate as compared with the rich variety, is due to its greater digestibility. In a more suitable ration, the rich variety would have been better utilised, and its inferiority is attributed to the nutritive ratio of the mixed food having been too wide.

N. H. J. M.

**Employment of Maize Cake for Feeding Cows.** By B. SCHULLE (*Ann. Agron.*, 1899, 25, 300; from *Fühling's Landw. Zeit.*, 1898, ii, 12).—Maize cake has the following percentage composition:

Water.	Proteids.	Fat.	N-free extract.	Fibre.	Ash.
10.28	19.5—26.9	8.1—16.2	39.0—43.1	10.26	2.37

Twelve cows were fed for three periods of twenty days each with rations containing (1) no maize cake, (2) 2 lbs., and (3) 4 lbs. of cake. The effect of cake was to slightly increase the yield of milk, but there was a decrease in the percentage and in the yield of milk fat. The cows, however, increased in weight under the influence of maize cake.

N. H. J. M.

**Effect of the Amount of Water in the Soil on the Amounts of Nitrogen and Ash in the Dry Matter of Plants.** By J. WILMS and CONRAD VON SEELHORST (*Chem. Centr.*, 1899, i, 444—445; from *J. Landw.*, 1898, 46, 413—426. Compare this vol., ii, 508).—The effect of water is greatest the more fertile the soil. Increased supply of water does not increase the yield of straw much more than of grain, and diminishes the percentage of nitrogen equally in grain and straw. Nitrogenous manure, with abundance of water, does not increase straw production exclusively, whilst excess of potash increases the straw and diminishes the amount of grain. The amount of ash and of potash in grain is increased when the water in the soil is increased, but after a certain point is reached, further addition of water has very little effect. The amounts of ash and potash in straw are also to some extent altered by the amount of water present in the soil. In the case of phosphoric acid, the variation in amount (both in grain and in straw) under the influence of varying amounts of soil-water is much less than is the case with potash; the phosphoric acid in the grain is first increased, then diminished slightly, whilst in straw there is generally an increase as the amount of soil-water increases. The manuring has considerable effect on the percentage of phosphoric acid in straw; in the grain, the amount of phosphoric acid is only higher when the yield of grain is diminished by a deficiency of any constituent (including phosphoric acid itself).

N. H. J. M.

**Dissemination of Ferments in the Soil.** By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1899, 25, 289—293).—Vetches were grown in large pots

containing different soils differently manured. The amounts of dry produce in grams (mean of two pots) were as follows:—

Vetch soil.		Vine soil.		
No manure.	Superphosphate.	No manure.	Superphosphate.	Dung.
56·0	63·8	74·5	78·5	89·5

The vine soil was therefore better than vetch soil. Superphosphate had very little effect, whilst farmyard manure gave a considerably increased yield. All the plants had root nodules, although the vine soil had not grown leguminous plants for twenty-four years.

The author believes that soil inoculation with nitragin or with alinit is unnecessary, since the microbes are usually already present in the soil. What is wanted is, not to increase the number of microbes, but to furnish conditions suitable to both plants and bacteria.

N. H. J. M.

**Phosphates [as Manures].** By JULES JOFFRE (*Bull. Soc. Chim.*, 1899, [iii], 21, 511—513).—The author has shown that apatite is far less soluble than tricalcium phosphate. He has made comparative experiments on mustard plants, using different phosphates as manures. Apatite has hardly any action, tricalcium phosphate has a decided effect, whilst monocalcium phosphate, being soluble in water, has a much greater effect.

R. H. P.

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## Analytical Chemistry.

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**Use of a Centrifugal Machine to Collect Precipitates in Quantitative Analysis.** By G. MEILLÈRE (*Bull. Soc. Chim.*, 1899, [iii], 21, 513—515).—The author recommends the use of a centrifugal machine in many quantitative operations where heavy precipitates are manipulated. It is shown that this method has many advantages, amongst others that very little liquid is required to wash the precipitates, that the danger of atmospheric oxidation is lessened, and that the calcination of the filter paper is avoided as the precipitates are weighed in the tube of the centrifugal machine. R. H. P.

**Standardisation of Volumetric Acid and Alkali.** By WILLIAM A. PUCKNER (*Pharm. Arch.*, 1898, 1, 172—184).—The investigation deals with the standardising of acids and alkalis with sufficient accuracy for pharmaceutical purposes.

Crystallised oxalic acid is not always of constant composition, and should be avoided. Sulphuric acid is recommended, its strength being ascertained by converting it into ammonium sulphate and weighing, as suggested by Weinig (*Abstr.*, 1893, ii, 145). This process has been variously criticised; the author, however, finds that it gives excellent results if conducted as follows: 10 c.c. of the approximately correct acid are measured into a wide, flat-bottomed weighing bottle

and weighed; the stopper is removed and 2 c.c. of strong ammonia free from residue are added; the whole is evaporated on a steam bath, the flask being rotated occasionally towards the end of the operation to avoid the formation of a crust which interferes with the drying; the residue is then finally dried to constant weight in a drying oven kept at a temperature of 65—80°; no loss of ammonia need then be feared.

Mineral acids may be standardised with borax, using methyl-orange as indicator. This substance being of high molecular weight is useful to those who have not a very delicate balance at their disposal, but the chief drawback is that the change in colour at the finish of the titration is not quite plain. Sodium carbonate is much more convenient if prepared as follows: 20 grams of pure sodium hydrogen carbonate are heated in a porcelain dish for 10 minutes over the full flame of a bunsen burner, the mass being well stirred so as to insure uniform heating; the partially cooled substance is then transferred to weighing tubes so that each shall contain 1.5—2.0 grams of the carbonate. When cold, the stopper is for a second removed, then reinserted and the tube weighed; the contents are emptied into a beaker and the tube is reweighed.

L. DE K.

**Detection Estimation of Small Quantities of Chlorine in Presence of Large Quantities of Bromine.** By HENRI BAUBIGNY (*Compt. rend.*, 1899, 128, 1326—1329).—About 6 grams of the potassium bromide to be examined are dissolved, together with 18 grams of crystallised cupric sulphate, in 110—120 c.c. of water, and 2.5 grams of potassium permanganate are added. The bromine liberated at the ordinary temperature is carried away by means of a current of air, and the liquid is gradually heated to 100° on a water-bath. After 10 minutes at this temperature, all odour of bromine has disappeared; 0.5 gram of permanganate is added to complete the oxidation, and the liquid heated until the vapour no longer reacts with fluorescein paper, care being taken, however, that the volume of the liquid is not reduced below 50 to 55 c.c. The chlorine in the residual liquid is precipitated in the usual way. Even the purest potassium bromide commercially obtainable contains 0.01 per cent. of chlorine (compare *Abstr.*, 1898, ii, 137, and this vol., ii, 244 and 328).

C. H. B.

**Separation and Estimation of Chlorine, Bromine, and Iodine in Halogen Salts.** By RICHARD JOS. MEYER (*Zeit. anorg. Chem.*, 1899, 21, 79—83).—An answer to Gooch and Browning's criticism (*Amer. J. Sci.*, 1890, [iii], 39, 188).

E. C. R.

**Estimation of Sulphuric Acid in the presence of Iron.** By FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1899, 21, 73—78).—An answer to Lunge's criticism on the authors' method. (See this vol., ii, 247 and 329).

E. C. R.

**Some Errors in the Estimation of Nitrogen.** By CYRIL G. HOPKINS (*J. Amer. Chem. Soc.*, 1898, 20, 961—965).—When estimating nitrogen as ammonia, two slight sources of error may occur. Loss of ammonia may take place when the delivery tube does not dip far enough into the standard acid; this may be prevented by using tubes reaching quite to the bottom of the receiving flasks and con-

tracted at the end to an aperture of 4 or 5 mm. diameter. Another source of error is caused by using standard ammonia and titrating in an open vessel, as the drops of liquid lose ammonia by evaporation before reaching the acid; this can be prevented by titrating in an Erlenmeyer flask attached to the burette by means of a rubber stopper provided with a capillary tube for relieving pressure.

L. DE K.

**Estimation of Hydrogen Phosphide in Mixtures of Gases.** By ALEXANDRE JOANNIS (*Compt. rend.*, 1899, 128, 1322—1325).—When hydrogen phosphide is brought in contact with a solution of cupric sulphate in such proportion that not more than 2 mols. of the sulphate are present for every 2 mols. of the gas, the absorption is at first slow, but afterwards becomes more rapid, and 1.5 mols. of the gas are absorbed for every 2 mols. of cupric sulphate present. Very soon, however, pure hydrogen phosphide is given off from the solution, and ultimately only 1 mol. of the gas is retained by every 2 mols. of the sulphate. If a further quantity of the copper salt is added at this stage, or if it is used in excess at first, the hydrogen phosphide is completely absorbed.

The cupric sulphate solution does not absorb nitrogen, hydrogen, methane, nitrous oxide, or nitric oxide, and they do not affect the absorption of the hydrogen phosphide. On the other hand, oxygen, carbonic oxide, and acetylene, if present, are absorbed in somewhat large quantity, doubtless because of their action on the cuprous salt that is formed by the reducing action of the hydrogen phosphide. Ethylene is similarly absorbed, but more slowly, and in smaller quantity.

It follows that hydrogen phosphide in mixtures of gases can only be estimated accurately by means of cupric sulphate solution in the absence of gases that have any action on cuprous salts, and in all cases it is essential to employ a higher proportion of the sulphate than 2 mols. for each molecule of hydrogen phosphide present. C. H. B.

**Estimation of Hydrogen Phosphide in Gaseous Mixtures.** By JOSEPH RIBAN (*Compt. rend.*, 1899, 128, 1452—1453).—With regard to Joannis's statement (preceding abstract) that, as an absorbent for hydrogen phosphide, copper sulphate solution is to be preferred to a hydrochloric acid solution of cuprous chloride, the author points out that the latter, when freshly prepared and colourless, does not attack mercury; cuprous chloride solution, when darkened by oxidation, may be readily decolorised by shaking with a little mercury. Further, copper sulphate solution, when used to dissolve hydrogen phosphide in a gaseous mixture, precipitates black, flocculent copper phosphide, from which it is difficult to separate the gaseous residue with accuracy.

T. H. P.

**Estimation of Calcium and Magnesium in Ashes.** By JOHN K. HAYWOOD (*J. Amer. Chem. Soc.*, 1899, 21, 508—511).—The usual process is to add an excess of ferric chloride and then to remove the phosphoric acid and the iron by boiling with ammonium acetate. The precipitate is, however, very bulky, and difficult to wash, and it also not unfrequently runs through the filter.

The author states that the washing may be entirely dispensed with by precipitating the iron in a 500 c.c. flask; when cold, water is added to the mark, and the mixture is well shaken, 250 c.c. are then filtered through a dry filter and the trace of iron which has redissolved is precipitated with a little ammonia; traces of manganese may be removed by adding more ammonia and some bromine. The filtrate then contains the calcium and magnesium.

This process does not give a correction for the volume of the ferric precipitate, but the author has proved that the accuracy of the result is not influenced by the volume of the precipitate unless it is inordinately large, which is rarely the case in practice. L. DE K.

**Quantitative Separation of Cerium.** By GRÉGOIRE N. WYROUBOFF and AUGUSTE VERNEUIL (*Compt. rend.*, 1899, 128, 1331—1334).—The method is based on the fact that cerosoceric oxide readily polymerises when heated with nitric acid, and that the sulphate  $4\text{Ce}_2\text{O}_3 \cdot 2\text{H}_2\text{SO}_4$  is quite insoluble in water. Difficulties are caused by the fact that the other monoxides can replace cerous oxide; moreover, it is not easy to completely convert the cerium into the cerosoceric oxide.

If the mixture of oxides contains more than 50 per cent. of cerosoceric oxide, it is dissolved in nitric acid to which successive small quantities of hydrogen peroxide are added. The concentrated solution of the nitrates is precipitated by ammonia and hydrogen peroxide, evaporated on a water-bath, and heated over a direct flame until ammonium nitrate begins to volatilise. The residue is dissolved in nitric acid, concentrated to a syrup, dissolved in water, heated to boiling, mixed with a small quantity of a 5 per cent. solution of ammonium sulphate, and the precipitate collected and converted into oxide by heating it at a white heat. The filtrate is mixed with ammonium persulphate and sodium acetate, and boiled, any further precipitate being treated as before.

If the mixture of oxides contains less than 50 per cent. of cerium, it is dissolved at once in nitric acid, evaporated to a syrup, and treated with the ammonium sulphate solution.

If the amount of cerium does not exceed 10 or 15 per cent., the first part of the operation may be omitted, and the nitric acid solution may be treated at once with ammonium persulphate and sodium acetate. C. H. B.

**Estimation of Iron in the Ferric State by Reduction with Sodium Thiosulphate and Titration with Iodine.** By JOHN T. NORTON (*Amer. J. Sci.*, 1899, 8, 25—30).—Attempts to estimate ferric salts by reduction with thiosulphate have already been made with varying success by Sherer, by Mohr, by Kremer and Landolt, and by Oudemans, who recommended the addition of a small quantity of copper sulphate; this process has been again modified by Haswell and also by Bruel.

The author, finding none of these processes to work satisfactorily, has carefully studied the reactions between ferric iron, free acid, and sodium thiosulphate, and now recommends the following process. It

is, however, only by exactly carrying out the instructions that very accurate results may be obtained.

An amount of ferric oxide not exceeding 0.2 gram is dissolved in hydrochloric acid and evaporated to a pasty mass. This is then dissolved in 800 c.c. of freshly boiled water, and, after adding a drop of solution of potassium thiocyanate, 50 c.c. of *N*/10 sodium thiosulphate are added and the liquid left until perfectly colourless; the excess of thiosulphate is then estimated as usual by means of *N*/10 iodine with starch as indicator. If it is preferred to work on a larger quantity of iron, which must, however, not exceed 0.4 gram, the amounts of water and thiosulphate must be increased in due proportion.

L. DE K.

**Syphon Arrangement for Reduction Flasks.** By HEINRICH GÖCKEL (*Zeit. angew. Chem.*, 1899, 620—621).—The apparatus is intended to prevent reoxidation of iron after a ferric salt has been reduced by means of nascent hydrogen.

The flask containing the ferric compound which is being reduced with metallic zinc is fitted with a cork through which passes a straight tube, the top of which is sealed to a narrow syphon whose longer limb dips into a solution of sodium hydrogen carbonate contained in a bulb which encircles and is sealed to the large tube.

When action has ceased, a little of the soda solution is drawn into the flask, but the excess of acid at once liberates carbonic anhydride which prevents more liquid from entering. The apparatus may now be left for a considerable time before the iron need be titrated.

L. DE K.

**Colorimetric Estimation of Nickel.** By MAURICE LUCAS (*Bull. Soc. Chim.*, 1899, [iii], 21, 432—433).—For the rapid approximate estimation of nickel in steel, the author makes use of the red coloration produced in alkaline or neutral solutions of nickel by potassium or ammonium thiocarbonate, a large excess of which must be added to obtain a uniform and persistent coloration. As copper and cobalt solutions also give colorations with thiocarbonates, these metals must be removed; the presence of cobalt is readily detected by the fact that the colour produced by ammonium thiocarbonate with cobalt salts is much darker than that obtained with the potassium salt. The process is carried out as follows: a graduated scale of tints is made by preparing a number of solutions of equal volumes containing equal quantities of the thiocarbonate to which have been added known and increasing proportions of nickel and about equal proportions of ammonium salts. 0.5 gram of the steel is then dissolved in nitrohydrochloric acid and the iron separated by two successive precipitations with ammonium chloride and ammonia solution; the liquid is then diluted to 500 c.c. Two separate quantities of 50 c.c. are taken and to one 10 c.c. of ammonium thiocarbonate solution are added, and to the other 10 c.c. of the solution of the potassium salt. If the former is much darker than the latter, cobalt is present and must be removed; but if not, the liquid is compared with the series of liquids containing known quantities of nickel.

T. H. P.

**Qualitative Separation of Antimony and Tin.** By G. BORNE-MANN (*Zeit. angew. Chem.*, 1899, 635—636).—The process is based on the insolubility of stannic phosphate in nitric acid, the antimony compound being readily soluble. The solution which must contain the tin and the antimony as perchlorides, and is, if necessary, heated with a little potassium chlorate, is mixed with a drop of solution of litmus or phenolphthalein, and aqueous caustic soda is added until a clear, strongly alkaline liquid is obtained; if tin is present, the precipitate redissolves but imperfectly unless heat is applied. After adding an excess of solution of disodium hydrogen phosphate, nitric acid is added in very slight excess and the mixture boiled. If a precipitate does not form, the liquid must be diluted and again boiled; the complete absence of any precipitate shows the absence of tin. In the presence of tin, a heavy precipitate of stannic phosphate is formed which, however, always occludes a trace of antimony and is, moreover, of varying composition; the filtrate contains nothing but antimony, which may then be proved by treatment with hydrogen sulphide.

L. DE K.

**Separation of Metals by Means of Hydrogen Bromide.** By ELIZABETH A. ATKINSON (*J. Amer. Chem. Soc.*, 1898, 20, 797—810).—Hydrogen chloride having been successfully employed by Moyer as a means of separating metallic oxides (*Abstr.*, 1897, ii, 434), the author has tried whether hydrogen bromide may be used instead with advantage.

The gas is readily prepared by dropping bromine from a separating funnel, at the rate of five drops a minute, upon anthracene contained in a flask placed in nearly boiling water. To purify the gas, it is passed first through a tube containing anthracene and then through one containing calcium chloride. The substance to be acted on is placed in a porcelain boat, which is then put inside a combustion tube connected with the receiver by a bent tube provided with a stopcock to avoid danger of backward suction. The volatile substances are collected in water except in the case of arsenic, where it is better to use dilute nitric acid. The heat may be obtained from three fish-tail burners.

The results obtained show that hydrogen bromide is a convenient reagent for quantitatively separating arsenic, bismuth, and antimony from metals the bromides of which are not readily volatile, such as copper, lead, cobalt, silver, and cadmium, but the separation of arsenic from iron is not satisfactory. The non-volatile bromides obtained are not always pure, as the lead compound has approximately the formula  $\text{PbO}_2 \cdot 5\text{PbBr}_2$ , and cobalt also forms an oxybromide, whilst copper yields cuprous bromide. The chlorides of antimony and bismuth require from 6 to 8 hours for their complete expulsion, but antimony bromide volatilises completely in  $1\frac{1}{2}$  hours, and bismuth bromide requires  $2\frac{1}{2}$  hours; arsenic chloride and bromide are both expelled in  $1\frac{1}{2}$  hours.

L. DE K.

**Measurements of Turbidity in Water.** By WILLIAM P. MASON (*J. Amer. Chem. Soc.*, 1899, 21, 516—517).—The sample is examined in a brass tube  $2\frac{1}{2}$  inches in diameter and 2 feet long,



closed at the ends by discs of  $\frac{1}{4}$  inch plate-glass held in place by screw caps. In a similar tube, distilled water is placed to which is then added an emulsion of very finely divided kaolin (1—1000) until the turbidity is the same as in the other. The turbidity may then be stated in parts per million.

Any material which subsides quickly should not be classed as turbidity, but as sediment, and should be collected and weighed.

L. DE K.

**Detection of Rare Metals in Mineral Waters.** By F. GARRIGOU (*Compt. rend.*, 1899, 128, 1587—1588).—The author finds that many mineral waters contain appreciable quantities of salts of the metals of the tin and iron groups, although these are not in general estimated. His method of detecting them is to calcine in a test-tube the residue obtained by evaporating two litres of the water. The mass is then boiled with hydrochloric acid, the liquor evaporated to dryness and to the cold residue dilute hydrochloric acid and hydrogen sulphide solution are added; if a darkening or coloration takes place, metals of the tin or copper group are present. If darkening only occurs on adding ammonia and ammonium sulphide solutions, metals of the iron group are indicated; the formation of a white turbidity, but no darkening, shows the presence of metals of the aluminium group, phosphates, borates, &c.

T. H. P.

**Estimation of Ferrocyanides and Carbonylferrocyanides and their Separation.** By JOSEPH AUGUSTE MULLER (*Bull. Soc. Chim.*, 1899, [iii], 21, 475—477).—A solution of ferrocyanide containing 4 to 5 grams per litre, is made slightly acid with nitric or acetic acid, a solution of lead nitrate or acetate added, and the precipitate formed after remaining for 12 hours filtered and dried; this is digested with sulphuric acid and then weighed. The weight of the mixture of lead sulphate and ferric oxide multiplied by 0.5378 gives the weight (as potassium ferrocyanide) of the ferrocyanide taken.

Carbonylferrocyanides are precipitated in a similar manner with copper acetate, the precipitate being ignited with sulphuric acid, and the copper in the residue estimated by Rose's method as cuprous sulphide. The weight of cuprous sulphide multiplied by 2.787 gives the corresponding weight of potassium carbonylferrocyanide.

The separation of these compounds is based on the fact that carbonylferrocyanides are not precipitated in acid solution by lead acetate, whilst the precipitation of ferrocyanides is quantitative. Any carbonylferrocyanide carried down in the precipitate is eliminated by solution in caustic soda and subsequent reprecipitation with dilute acetic acid. The carbonylferrocyanide is then estimated by precipitation with copper acetate.

R. H. P.

**Estimation of Sugars by Weighing the Copper Precipitate.** By G. MEILLÈRE and PH. CHAPPELLE (*Bull. Soc. Chim.*, 1899, [iii], 21, 515).—The reduction of the Fehling's solution is carried out in a tube of the centrifugal machine (this vol., ii, 610). The tube is heated in brine and centrifugated. After two washings, the tube is heated for 5 minutes at 150°, cooled, and then weighed. The result can be controlled by reducing the cuprous oxide in the same tube by a current

of hydrogen. Some kinds of glass are in this procedure attacked by the alkaline liquids; it is therefore advisable to weigh the tube before and after the estimation.

R. H. P.

**Iodometric Estimation of Sugar by means of Fehling's Solution.** By N. SCHOORL (*Zeit. angew. Chem.*, 1899, 633—635).—The process is a modification of the iodometric method of estimating the excess of copper left in the liquid after treatment with a reducing sugar, which was first proposed by Lehmann and improved by Riegler and also by Maquenne.

10 c.c. of Fehling's solution of copper sulphate are mixed in a 200 c.c. Erlenmeyer flask with 10 c.c. of Fehling-Soxhlet's alkaline solution of Rochelle salts, diluted with 50 c.c. of water, and boiled for 2 minutes. After cooling rapidly under a tap, 10 c.c. of a 20 per cent. solution of potassium iodide are first added, and then 10 c.c. of a 25 per cent. solution of sulphuric acid, the liberated iodine being then titrated without delay with *N*/10 sodium thiosulphate.

The experiment is then repeated after having first added a quantity of dextrose or invert sugar not exceeding 0.090 gram, or about 0.125 gram of lactose; when dealing with the latter sugar, the time of boiling should be extended to 5 minutes, and the blank experiment conducted in the same way. The difference in the number of c.c. of thiosulphate used in the two experiments is the measure of the amount of sugar. A convenient table is given showing the relation between the thiosulphate and the lactose, dextrose, saccharose, and starch.

L. DE K.

**Assay of Spirit of Nitrous Ether.** By RICHARD FISCHER and J. A. ANDERSON (*Pharm. Arch.*, 1898, 1, 161—167, 169—172).—The authors have investigated the three principal methods in use for the assay of spirit of nitrous ether, U.S.P.

The gasometric, or Allen's, method is the most convenient, but to obtain correct results, due corrections must be made for pressure, vapour tension, and solubility of the nitric oxide in the brine; these corrections are given in tables. An important fact is stated, namely, that the gas given off on mixing the sample with water or potassium iodide may consist principally of the vapour of ethylic nitrite; even the gas given off in the nitrometer by treatment with potassium iodide and sulphuric acid often contains a considerable proportion of ethylic nitrite vapour; as this, however, represents its own volume of nitrogen at an average temperature, it does not affect the experiment; when cooled to zero, it practically disappears.

The process based on heating the sample with a small quantity of potassium hydroxide and afterwards titrating the nitrite formed by means of potassium iodide and sodium thiosulphate, gives untrustworthy results, but by using more alkali, and warming for at least 24 hours, good results may be obtained.

Curtman's process is also criticised. This consists in treating the sample with ferrous sulphate, expelling the nitric oxide by heating, and estimating by the iodometric method the ferric iron produced. The authors find this process to be quite valueless, but by operating in an atmosphere of carbonic anhydride, and extending the time of action from

half-an-hour to 5 hours, or even some days, results may be obtained agreeing closely with those given by Allen's method. L. DE K.

**Assay of Amylic Nitrite.** By RICHARD FISCHER and J. A. ANDERSON (*Pharm. Arch.*, 1898, 1, 189—194).—The author recommends preparing amylic nitrite by following the directions of the U.S.P. For the purpose of testing, a 5 per cent. alcoholic solution may be prepared. The best and quickest results are obtained by the gasometric method (see preceding abstract) and special tables are given. The other processes as modified by the authors may also be used, but they take from 1 to 2 days. L. DE K.

**Estimation of the Acidity of Tanning Liquors.** By PAESSLER and SPANJER (*Zeit. angew. Chem.*, 1899, 636—638).—Twenty-five c.c. of the infusion is mixed in a beaker with 25 c.c. of a neutral solution of gelatin (2:1000, but if the material is rich in tannin, a stronger gelatin solution may be employed). Standardised baryta water is then added from a burette until the liquid shows neutrality when dropped on delicate litmus paper. The acidity is calculated as acetic acid. The accuracy of the process has been proved by testing mixtures of freshly prepared tannin infusions with known amounts of acetic or lactic acids; the results were very satisfactory. L. DE K.

**Estimation of added Water in Milk.** By A. G. WOODMAN (*J. Amer. Chem. Soc.*, 1899, 21, 503—508).—The author's process is a slight modification of the method proposed by Radulesen, which is based on the fact that milk serum has a fairly constant specific gravity.

One hundred c.c. of the sample, which should be at a temperature of about 20°, are thoroughly mixed with 2 c.c. of dilute acetic acid of sp. gr. 1.035. The beaker containing the mixture is covered with a watch glass and heated for 20 minutes in a water-bath at 70°, when it is removed and at once placed in ice water, where it is kept for 10 or 15 minutes, and the liquid then passed through a dry folded filter. The filtrate, which should be clear, or but very slightly opalescent, is cooled to 15°, and the sp. gr. taken, say, with a Westphal balance; if the sample is pure this should not be less than 1.029 (according to Radulesen, 1.027 is the limit) and the percentage of added water may therefore be readily calculated from a deficiency in gravity. The average decrease in sp. gr. for each 10 per cent. of water is 0.0031.

L. DE K.

**Action of Silver Nitrate on the Fatty Acids of Cotton Seed Oil.** By EUGÈNE CHARABOT and MARCH (*Bull. Soc. Chim.*, 1899, [iii], 21, 552—554).—The fatty acids obtained by the hydrolysis of cotton seed oil and subsequent precipitation with a mineral acid contain sulphur compounds. Silver nitrate gives with these acids a brown precipitate of the silver salt of an acid (melting at 52°) mixed with silver sulphide. The reaction must be used with care to detect cotton seed oil in olive oil, as the latter, under similar conditions, gives a black precipitate of silver sulphide (Dupont, *Abstr.*, 1896, i, 409).

R. H. P.

**Estimation of Morphine in Opium.** By CLEMENTE MONTE-MARTINI and D. TRASCIATTI (*Gazzetta*, 1899, 29, i, 292—300).—A discussion of various criticisms on the method given by the authors for the estimation of morphine in opium (*Abstr.*, 1898, ii, 270).

T. H. P.

**Estimation of Santonin.** By JULIUS KATZ (*Arch. Pharm.*, 1899, 237, 245—256).—Ten grams of the coarsely-powdered *Flores Cinæ*, are extracted with ether (*Pharm. Ger.*, III) for 2 hours in a Soxhlet apparatus. The ether is distilled off, and the residue is boiled for  $1\frac{1}{4}$ — $1\frac{1}{2}$  hour in a reflux apparatus with a solution of 5.0 grams of crystallised barium hydroxide in 100 c.c. of water. The solution is allowed to cool, and is then saturated with carbonic anhydride, until it reddens blue litmus paper; it is then filtered at once, and washed twice, each time with about 20 c.c. of water. The filtrate is concentrated on the water-bath to a volume of about 20 c.c., mixed with 10 c.c. of dilute (12.5 per cent.) hydrochloric acid, warmed for 2 mins. more (no longer), allowed to cool, and poured into a separating funnel, any crystals of santonin that remain in the basin being rinsed into the funnel with about 20 c.c. of chloroform. The mixture in the funnel is then shaken well, and the chloroform solution is drawn off and filtered, dish, funnel, and filter being washed twice with about 20 c.c. of chloroform. The chloroform is then distilled off, and the residue boiled for 10 mins. in a reflux apparatus with 50 c.c. of 15 per cent. alcohol; the hot solution is filtered into a weighed flask, the apparatus employed being rinsed twice into the flask with 10 c.c. of boiling 15 per cent. alcohol, after which the flask is covered with a watch-glass and set aside for 24 hours. The flask is then weighed; the contents are filtered through a weighed filter of 9 cm. diameter (any milkiness in the filtrate, due to resinous matter, being neglected), and flask and filter are washed with 10 c.c. of 15 per cent. alcohol; the filter is dried in the flask, and the latter is weighed. For every 10-grams of the alcoholic filtrate, excluding the last 10 c.c., 0.006 gram must be added to the weight of santonin found, to correct for the solubility of the latter in the alcohol. In two test experiments 0.2640 and 0.2834 gram of santonin were obtained instead of 0.2770 and 0.2862 taken.

A modification of the above process may be introduced, owing to the fact that santonin only reacts with alcoholic potash at 80—90°, whereas the accompanying resin does so at the ordinary temperature. The solution in 15 per cent. alcohol is evaporated, the residue is dissolved in 20—30 c.c. of absolute alcohol, 3 drops of phenolphthalein are added, and then *N*/10 potash solution until the pink colour is permanent for 10 minutes. At this point, 20 c.c. of *N*/10 potash are added at once, the solution is heated to boiling, diluted with 50 c.c. of cold water, and titrated with *N*/10 hydrochloric acid. A blank experiment is performed to ascertain the effect of the glass on the potash. From the 20 c.c. are subtracted the volume of acid used, and of potash neutralised in the blank experiment, and the remainder is multiplied by 0.0246, which gives the weight of santonin present. In an experiment made to test the possibility of titrating santonin in alcoholic solution, 0.3100 gram were found instead of 0.3080 taken. In another

experiment, 3.21 and 3.38 per cent. were found, as against 3.16 by the gravimetric method.

From pastilles that contain only sugar in addition, santonin can be obtained in a state of sufficient purity by simple extraction with chloroform. When chocolate also is present, the method described above must be followed, except that the chloroform solution may be simply evaporated to dryness (more easily if a little ether be added) and the residue weighed. Should a slight turbidity of the filtered barium santonate solution indicate the presence of traces of fatty acids, the crystals of santonin may be washed from these with 10—20 c.c. of light petroleum, in which they are almost insoluble.

In 10 samples of *Flores Cinæ* the percentage of santonin was found to range from 1.21 to 3.16; in the tincture prepared from these by percolation with five times their weight of 90 per cent. alcohol, it ranged from 0.212 to 0.628.

C. F. B.

### Testing Indigo : A Yellow Compound found in Java Indigo.

By CHRISTOPHER RAWSON (*J. Soc. Chem. Ind.*, 1899, 18, 251—252).—The usual plan of assaying indigo is to dissolve the sample in strong sulphuric acid; on adding water, the colouring matter remains in solution as indigotindisulphonic acid, and various impurities remain in suspension. Before titrating, it is necessary to remove these insoluble matters, but the filtration is very troublesome and part of the colouring matter is fixed by the paper. The use of paper may be avoided, as follows: 0.5 gram of the powdered sample, mixed with glass powder, is digested with 25 c.c. of pure, strong sulphuric acid at 70° for 1 hour. When cold, the liquid is diluted with water, mixed with 10 c.c. of a 20 per cent. solution of barium chloride, and diluted to 500 c.c. In about 20 minutes, the barium sulphate which carries down all the suspended matter will have settled, and an aliquot part of the clear solution may be drawn off with a pipette.

The presence of a yellow colouring matter, sometimes to the extent of 20 per cent., has recently been noticed in samples of Java indigo, and the presence of this substance interferes with the ordinary method of analysis, as it behaves in many respects like indigotin. It may be detected by adding aqueous soda or ammonia to powdered indigo placed in a porcelain basin, when the alkali will assume a deep yellow colour. It may be removed by boiling with dilute ammonia, or preferably with alcohol, which also dissolves any indirubin, and the insoluble matter is then sulphonated as usual and titrated for indigotin. The alcoholic or ethereal solutions are colourless, but turn yellow with alkalis. Indirubin may be estimated as follows: 0.1—0.25 gram of the sample is boiled with 150 c.c. of ether in a reflux apparatus; when cold, the liquid is made up to 200 c.c. and shaken with 10 c.c. of water; this causes the undissolved matter to settle completely. A measured quantity of the liquid is now withdrawn and compared in a colorimeter with a standard solution of indirubin.

L. DE K.

## General and Physical Chemistry.

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**Refraction of Pure Water and of Normal Salt Solutions.—I. Water.**—By CARL BENDER (*Ann. Phys. Chem.*, 1899, [i], 68, 343—349).—The refraction of water was determined at various temperatures by a Pulfrich's refractometer and three interpolation formulæ are given for the values of the refraction for  $H_\alpha$ ,  $H_\beta$ , and  $H_\gamma$ . The dispersion decreases only very slightly with rise of temperature, so that between  $10^\circ$  and  $40^\circ$  similar formulæ differing only in the first term may be used for the three lines—namely,  $H_\alpha = 1.3323004 - 0.0001129 (t^\circ/5) - 0.0000419 (t^\circ/5)^2$ , the first terms for  $H_\beta$  and  $H_\gamma$  being respectively 1.3382118 and 1.3414389. The values for water containing dissolved air were found to agree with those of pure water within the limits of experimental error.  
L. M. J.

**Changes of Silver Iodide in Light, and the Daguerreotype Process.** By HERMANN SCHOLL (*Ann. Phys. Chem.*, 1899, [ii], 68, 149—182).—If a silvered glass is exposed to iodine vapour, it becomes covered with a clear deposit of silver iodide, which, on exposure to light, becomes cloudy. The author shows that this cloudiness is not due to any chemical change, but to a mechanical alteration of the illuminated layer; and the change further requires the catalytic action of some oxidising agent such as oxygen or iodine. If the silver iodide has an underlayer of silver, however, chemical action ensues and the silver becomes converted into iodide with reduction of the surface layers; this action is also accelerated by the catalytic action of the oxygen of the air. The capability of development of exposed Daguerreotype plates is due to this change and to the presence, in the surface layers, of the reduced silver; it extends also through the whole thickness and is throughout proportional to the light intensity at the surface. A layer of silver iodide was deposited between two platinised glass plates and connected electrically with a galvanometer, and when this was exposed to light an E.M.F. was produced the direction of which indicated a migration of iodine in the direction of the light rays.  
L. M. J.

**Contributions to the Study of Optical Isomerism.** By PAUL WALDEN (*Chem. Centr.*, 1899, i, 327; from *J. Russ. Chem. Soc.*, 1898, 30, 767—794).—A continuation of earlier work (compare this vol., ii, 393). This section deals with Guye's hypothesis. The author gives a general account of his own publications, and quotes Guye, Landolt, and Ostwald as supporting his conclusions. The theory of Le Bel and van't Hoff, that only a chemical difference in the four groups attached to the carbon atom is necessary for the production of asymmetry, is regarded as entirely confirmed. The following molecular rotations are given in the paper :—

<i>l</i> -Amylic propionate .....	[M] <sub>D</sub> + 3·96°	<i>l</i> -Amylic oxalate .....	[M] <sub>D</sub> + 11·78
„ butyrate .....	4·43	„ malonate .....	8·09
„ bromacetate .....	5·75	„ ethylmalonate .....	9·26
„ bromopropionate .....	5·41	„ isoamylmalonate .....	9·98
„ glycollate .....	3·67	„ glutarate .....	9·54
„ α-hydroxybutyrate .....	4·82	„ suberate .....	8·76
„ α-hydroxyisobutyrate .....	5·06	„ sebacate .....	9·18

J. C. P.

**Molecular Refraction and Dispersion and Specific Rotation of Compounds of Camphor and Aromatic Aldehydes.** By ALBIN HALLER and PAUL TH. MULLER (*Compt. rend.*, 1899, 128, 1370—1373).—The optical properties of compounds of the type

$C_8H_{14} \begin{smallmatrix} & C:CHR \\ & | \\ & CO \end{smallmatrix}$ , in which R represents radicles derived from benzaldehyde, cinnamaldehyde, piperonaldehyde, and the methoxybenzaldehydes, are summarised in the table:—

R.	Molecular Refraction.						Molecular dispersion.		Specific rotation.
	$\alpha$ .	Calculated (Brühl).	Na.	Calculated (Conrady).	$\beta$ .	$\gamma$ .	Found.	Calculated (Brühl).	
•Ph .....	76·35	71·94	77·21	72·65	79·35	82·70	6·35	2·39	+425·11°
•C <sub>6</sub> H <sub>4</sub> $\begin{smallmatrix} \diagup O \diagdown \\ \diagdown \diagup \end{smallmatrix}$ CH <sub>2</sub> .....	85·23	77·61	86·00	78·52	89·30	93·17	7·94	2·46	435·40
•C <sub>6</sub> H <sub>4</sub> Pr $\beta$ .....	90·80	85·65	91·43	86·46	94·93	98·15	7·35	2·73	495·68
•C <sub>6</sub> H <sub>4</sub> •OMe [1 : 2] .....	83·03	78·16	83·96	78·94	86·73	89·43	6·40	2·51	431·50
•C <sub>6</sub> H <sub>4</sub> •OMe [1 : 3] .....	83·42	78·16	84·09	78·94	86·87	89·28	5·86	2·51	379·35
•C <sub>6</sub> H <sub>4</sub> •OMe [1 : 4] .....	85·20	78·16	86·02	78·94	89·50	92·66	7·46	2·51	467·07

The calculated values (employing Brühl's and Conrad's coefficients as indicated in the table) are based on the assumption that the group >C:CHR contains four double linkings, and the conclusion is drawn that the introduction of this radicle augments the molecular refraction and dispersion of camphor, and multiplies the value of its specific rotation by ten (compare Gladstone, *Trans.*, 1891, 590).

G. T. M.

**Dissipation of Electrostatic Charges by Light.** By OSCAR KNOBLAUCH (*Zeit. physikal. Chem.*, 1899, 29, 527—545).—Many negatively charged substances, when illuminated, gradually lose their charge, as may be shown by connecting them with an electrometer. The author has examined numerous substances in this way, and finds that those which are sensitive to light have a special tendency to lose an electrostatic charge. The discharged electricity must be conveyed by ions either of the substance itself or of the superficially absorbed oxygen. Only negative charges are lost by dissipation, hence the discharged ions must be negative whether the substance is metal, sulphur, or glass. The author accordingly regards the dissipation as

depending on an oxidation process, the loss of charge being effected by negative oxygen ions. In accordance with this view, oxidisable substances, such as sulphides and photographic developers, are found to lose their charges under the influence of light, whilst highly oxidised substances like sulphates and permanganates are not affected. The fact that certain substances such as zinc take a positive charge when illuminated may be similarly explained. The oxidation of phosphorus is an analogous phenomenon.

J. C. P.

**Dielectric Constants and Aggregation Changes of Alcohols at Low Temperatures.** By RICHARD ABEGG and W. SEITZ (*Zeit. physikal. Chem.*, 1899, 29, 242—248).—Abegg has shown that the temperature coefficient of the dielectric constant is given by the expression  $-dD/dT = D/190$ , that is  $D = ce^{-T/190}$  (Abstr., 1897, ii, 240). To more completely test this expression, determinations of the constant were made for amyllic, isobutylic, propylic, ethylic, and methylic alcohols at temperatures reaching  $-140^{\circ}$ , the constant low temperatures being obtained by employing baths of boiling ammonia, solid carbonic anhydride and ether, or melting chloroform, toluene, ether, or ethylic bromide. The results are in very fair accord with the values calculated from the formula. In each case, when the alcohol freezes a sudden drop occurs in the constant, and there appears to be no difference between the value for the glassy mass and the crystals, so that no evidence of a continuous change was obtained. The above formula differs from that calculated from either of the refraction formulæ, but it has been shown that the coefficients so calculated are not in accord with the experimental numbers (Ratz, Abstr., 1896, ii, 288; Philip, Abstr., 1898, ii, 9). It is noteworthy that, notwithstanding the complexity of liquid alcohol molecules, the dielectric constant obtained is identical with that for nitrobenzene, so that any connection between complexity and dielectric constant appears doubtful.

L. M. J.

**Dielectric Behaviour of a Crystalline Liquid.** By RICHARD ABEGG and W. SEITZ (*Zeit. physikal. Chem.*, 1899, 29, 491—493).—When a compound passes from the liquid to the solid state, there is a sudden fall in the specific inductive capacity. An example of change from a homogeneous to a crystalline liquid is furnished by 1:4-azoxyanisole, and it is shown that the change is not accompanied by any alteration in the value of the specific inductive capacity, apart from the gradual increase of the latter with falling temperature. When the azoxyanisole solidifies, there is a sudden fall in the value of the specific inductive capacity from 4.3 to 2.3. These experiments show that when a liquid ceases to be homogeneous and becomes crystalline, there can be no separation of solid substance; this is in accordance with Schenck's views.

J. C. P.

**Conductivity of Fused Zinc Chloride.** By HERMANN S. SCHULTZE (*Zeit. anorg. Chem.*, 1899, 20, 333—339).—The varying results obtained by different investigators of this subject may be due to the difficulty of freeing zinc chloride from the last traces of water. The author has accordingly determined the conductivity of carefully



dehydrated zinc chloride through a considerable range of temperature. The specific conductivity is 0.460 (ohm and cub. cm.) at 700°, and falls with the temperature, the rate of fall increasing at lower temperatures.

J. C. P.

**Differences of Potential between Metals and Non-aqueous Solutions of their Salts.** By LOUIS KAHLENBERG (*J. Physical Chem.*, 1899, 3, 379—403).—Although the osmotic theory of the voltaic cell has led to many measurements of potential differences in aqueous solutions, but few experiments have been made with other solvents, and these have indicated that the solution tension of a metal is dependent on the solvent in which it is immersed (compare Jones, *Abstr.*, 1894, ii, 374). The author has therefore determined the E.M.F.'s of a large number of electrodes consisting of the metal immersed in a *N*/10 solution of one of its salts in solvents other than water, those employed being methylic, ethylic, and benzylic alcohols, glycol, glycerol, pyridine, piperidine, acetone, aniline and its alkyl derivatives, quinoline, various amines, and nitrobenzene. In the case of silver electrodes, 46 E.M.F. determinations were made, and it was found that the potential differences between the metal and solution differ greatly with the solvent employed, varying from 1.2 volts in the case of acetone to 0.36 volt in propylamine; the value in aqueous solution is 0.56 volt. In all cases, the silver is positive to the solution. In groups of solvents of similar chemical nature—as, for example, the alcohols, the aliphatic amines, the amidobenzenes, &c.—the differences of potential are approximately equal, this being more marked the closer the relationship of the solvents. In the case of magnesium electrodes, the difference of potential between the metal and the *N*/10 solution in pyridine or aniline is about 0.4 volt, whilst in aqueous solution the difference is 1.06 volts, the metal being negative. The metal is hence more positive, or less negative, to the pyridine solution than to the aqueous solution, whereas the converse holds for silver. Zinc also is less negative to pyridine, aniline, quinoline, or alcohol solutions than to aqueous; in the quinoline solution, the zinc is actually positive to the solution. Cadmium and thallium show very little difference between the aqueous and pyridine solutions, lead is more positive, and copper less positive to solutions in pyridine than to those in water. The difference of potential between iron and the *N*/10 solution of ferric chloride in water is 0.031 volt, but for solutions in alcohol, nitrobenzene, and orthonitrotoluene the differences amount to more than 1 volt. If platinum is used in place of iron as the electrode, so that the chain becomes one of reduction, the differences are in the opposite sense, the metal being most positive to the aqueous solution.

These results are discussed in the light of the osmotic theory of electromotive force. For the same metal in different solutions, the E.M.F. is proportional to  $\log. P/p$ , where  $P$  is the solution tension, and  $p$  the ionic pressure, which is again proportional to the dissociation, and it is evident from the above results that  $P$  must vary greatly with different solvents, and that the nature of the variation differs for different metals. Even if this supposition is made, how-

ever, other difficulties arise, as many salts yield solutions in pyridine which possess considerable conductivity, and in which Faraday's electrolytic laws are valid, although cryoscopic measurements indicate that no dissociation occurs (compare Werner, *Abstr.*, 1898, ii, 214). The author therefore considers that the whole osmotic theory of electromotive force and conductivity is, at any rate, quite insufficient when applied to solvents other than water. L. M. J.

**The Ions of Dilute Sulphuric Acid.** By WILHELM STARCK (*Zeit. physikal. Chem.*, 1899, 29, 385—400).—At high concentrations, the  $\text{H}_2\text{SO}_4$  molecule dissociates chiefly into  $\overset{+}{\text{H}}$  and  $\overset{-}{\text{HSO}}_4$ , at low concentrations into  $\overset{+}{\text{H}}$ ,  $\overset{+}{\text{H}}$ , and  $\overset{-}{\text{SO}}_4$ ; hence the migration number of the sulphuric acid anion decreases with increasing dilution. The proportion of  $\text{H}_2\text{SO}_4$  molecules which dissociate into  $\overset{+}{\text{H}}$  and  $\overset{-}{\text{HSO}}_4$  would probably, on kinetic grounds, fall with rising temperature. The formation of persulphuric acid runs parallel with the presence of  $\text{HSO}_4$  ions up to a certain concentration (40 per cent. acid). The poorer yield of persulphuric acid from this point onwards is probably due to its instability in concentrated sulphuric acid solution, rather than to a decrease in the quantity of  $\text{HSO}_4$  ions. The formation of persulphuric acid is favoured by fall of temperature, and this would agree with the probable increase of  $\text{HSO}_4$  ions as the temperature falls.

The author has determined the migration number of the sulphuric acid anion at various concentrations and at various temperatures, and finds, in general agreement with Hittorf and Wiedemann, an increase of the migration number with increasing concentration. The influence of temperature is contrary to expectation, and the temperature coefficient is approximately the same for higher concentrations as that found by Bein (*Abstr.*, 1898, ii, 553) for low concentrations, namely, about 1/100. The increase of the migration number with the temperature is not to be attributed to a larger formation of the more complex ion, but probably to a decrease of the frictional resistance experienced by the ions. J. C. P.

**Ionic Velocities.** By ORME MASSON (*Zeit. physikal. Chem.*, 1899, 29, 501—526; *Phil. Trans.*, 1899, 192, A, 331—350).—The doubtful validity of Lodge's method, and the narrow scope of Whetham's, have led the author to devise a new method of measuring directly the velocity of ions. Two flasks, each provided with a lateral opening, are connected by a graduated horizontal tube containing a mixed solution of gelatin and the salt to be investigated (compare Masson and Steele, *Trans.*, 1899, 75, 726). The flasks contain suitable solutions in which the electrodes dip. These anode and cathode solutions must both be distinctly coloured, the coloured ion being the cation in the anode solution, and the anion in the cathode solution. Further, the coloured ions must migrate at a specifically slower rate than the corresponding ions of the salt in the tube. A suitable anode solution is copper sulphate with a copper anode; a suitable cathode solution is sodium chromate with a platinum cathode.

When a current passes, the progress of the cations (for example, K) in the colourless gelatin solution is accompanied by an equal advance of the blue Cu ions: the anions (for example, Cl) are similarly followed by the yellow  $\text{CrO}_4$  ions. The contents of the tube thus become blue at one end, colourless in the middle, and yellow at the other end. The relative length of the blue and yellow parts gives the ratio of the velocities of cation (K) and anion (Cl); from this ratio, the migration numbers can be calculated and compared with the values found by Hittorf.

The method depends essentially on the supposition that the progress of the coloured ions is determined by the velocity of the colourless ions in front. Analysis showed that the bounding plane between coloured and colourless zones was very sharp. The relative length of the blue and yellow parts remains constant throughout one experiment and is the same for different experiments at the same concentration. The ratio of the ionic velocities for the same salt is the same when potassium ferrocyanide or potassium tartrate is substituted for sodium chromate. Theory, too, excludes any mixture of the ions, provided that the coloured ions are specifically slower than the colourless ions which precede them.

The migration numbers for the anion obtained from the ratio of the ionic velocities are, in the case of sodium, potassium, and ammonium salts, smaller than those found by Hittorf, whose values, however, hold for more dilute solutions than those used by the author. Contrary to Hittorf's observation, the migration number for the Cl ion seems to decrease slightly with increasing concentration. The relative velocities of the ions are compared with Kohlrausch's numbers, and a good agreement is found: the absolute velocities are smaller than in aqueous solution.

J. C. P.

**Theory of the Formation of Nickel Sulphide.** By J. LIVINGSTON R. MORGAN and A. H. GOTTHELF (*J. Amer. Chem. Soc.*, 1899, 21, 494—502).—Nickel sulphide, as precipitated from alkaline solutions by hydrogen sulphide, is insoluble in dilute acids, but, nevertheless, it is not precipitated by hydrogen sulphide from solutions containing insufficient acid to dissolve the sulphide already formed. This anomalous behaviour is attributed to the fact that a saturated solution of nickel sulphide has a slightly lower concentration of negative sulphide ions ( $\text{S}^{--}$  or  $\text{HS}^{--}$ ) than a saturated solution of hydrogen sulphide, so that on adding a little acid to the latter, this concentration becomes increased to nearly that of the nickel sulphide solution. Hence the compound already present (nickel sulphide or hydrogen sulphide) remains practically unchanged, the velocity of change being proportional to the difference in concentration of the two with respect to the negative ions. These views are supported by the fact that nickel sulphide is formed in the presence of a large amount of acetic acid, or of a small amount of hydrochloric acid, whilst, with neutral solutions, such as nickel dichloracetate, precipitation of the sulphide goes on until the concentrations of the negative ions of the hydrogen sulphide and the nickel sulphide become equalised. A quite analogous explanation holds for the similar behaviour of cobalt sulphide.

The solubility of zinc sulphide in dilute hydrochloric acid, in which the sulphides of nickel and cobalt are insoluble, is due to the almost complete ionisation of the chlorides of nickel and cobalt, the formation of a small quantity of chloride preventing the production of more; with zinc, however, the ionisation of the chloride is less, and the effect of this is increased by the removal of zinc ions from the solution by hydrolytic dissociation.

T. H. P.

**Theory of the Separation of Barium, Strontium, and Calcium from the Mixed Sulphates.** By J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1899, 21, 522—527).—Ammonium carbonate, or a mixture of a soluble sulphate and carbonate, transforms strontium and calcium sulphates into carbonates, leaving barium sulphate unchanged. From the solubilities of the sulphates and carbonates of barium, strontium, and calcium, the ionic concentrations are calculated, and it is found that, with strontium and calcium, the carbonates are less soluble than the sulphates, whilst with barium the converse holds. In order that any sulphate may be transformed into carbonate, sufficient  $\text{CO}_3$  ions must be present to cause the solubility product of the carbonate to be reached in a saturated solution of the sulphate; in the case of barium, no sulphate is formed until the concentration of the  $\text{CO}_3$  ions is at least 0.00115 gram-mol. per litre, the corresponding numbers for strontium and calcium being respectively 0.0000092 and 0.000000385. The  $\text{SO}_4$  ions of the alkali sulphate, formed by the transformation, decrease the solubility of the insoluble sulphate, a condition of equilibrium being attained unless a sufficient excess of  $\text{CO}_3$  ions are present. For the solubility product of barium carbonate to be reached in a 1/10 normal solution of  $\text{SO}_4$  ions, the concentration of  $\text{CO}_3$  ions must be at least that of a 10.5 normal solution; with strontium and calcium, this effect of the  $\text{SO}_4$  ions is smaller, in the case of the former, a 0.0017 normal solution of the  $\text{CO}_3$  ions being necessary in order that the solubility product of the carbonate may be reached. Hence, in a mixture of barium, strontium, and calcium sulphates, the strontium and calcium compounds are rapidly transformed into carbonates, whilst with barium sulphate, although it may also dissolve slightly, yet the soluble sulphate formed during its solution soon prevents any further reaction, and that formed from the strontium and calcium salts causes the reverse transformation to take place.

T. H. P.

**Electrolytic Dissociation and Toxic Effect.** By J. F. CLARK (*J. Physical Chem.*, 1899, 3, 263—316).—Fungi, when subjected to the action of deleterious agents, offer in general much more resistance than the higher plants. The hydroxyl ion  $\text{OH}^-$  is rather more toxic to moulds than  $\text{H}^+$ . The toxic value of the ions  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  increases slightly with the atomic weight. The cyanogen radicle is a very powerful poison to fungi, potassium cyanide having nine times the toxic effect of hydrochloric acid. Mercuric chloride and silver nitrate are about equally toxic to moulds, and are followed closely by potassium dichromate, potassium chromate, and formaldehyde. Dissociation in many cases lessens the toxic action. Out of eight acids examined, six were more toxic in the molecular form than after dissociation. The toxic effect of the undissociated molecule of acetic

acid is 2·8 times that of  $\overset{+}{\text{H}}$ , while the undissociated HCN molecule has a toxic value 76·6 times that of  $\overset{+}{\text{H}}$ . When hydrogen in acetic acid is replaced by chlorine, the toxicity increases, but the dissociation increases also: the two effects partially balance each other, and the relative toxic action of the chloracetic acids depends on the concentration. The anions of the mineral acids HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  have a low toxic value for fungi, less than one thirty-second of that for  $\overset{+}{\text{H}}$ .

J. C. P.

**Neutralisation, Solution, and Electrolysis.** By GUSTAV PLATNER (*Chem. Centr.*, 1899, i, 466; from *Electrochem. Zeit.*, 5, 199—205).—The combination of a hydrogen atom with an oxygen atom liberates 34·15 Cal.; the view that the union of a hydrogen atom with a hydroxyl group liberates 13·7 Cal. is regarded as incorrect.

When a metal is dissolved in acid, it first forms a hydroxide with the hydroxyl of the water or of the acid, and the hydroxide reacts with the acid. When an anhydrous salt is dissolved, water is first decomposed; the hydroxide formed from the metal of the salt and the hydroxyl of the water neutralises the acid simultaneously formed. When the process is resolved into these stages, heats of solution can be calculated, agreeing well with those observed. The author regards his conceptions as able to replace the electrolytic dissociation theory.

J. C. P.

**Aqueous Solutions of Double Salts. III.** By HARRY C. JONES and NICHOLAS KNIGHT (*Amer. Chem. J.*, 1899, 22, 110—141).

—The authors have extended the experiments of Jones and Mackay (*Abstr.*, 1897, ii, 396) and Jones and Ota (this vol., ii, 587) by studying the conductivity of solutions of the double chlorides,  $2\text{NaCl}, \text{ZnCl}_2 + 3\text{H}_2\text{O}$ ;  $\text{SrCl}_2, 2\text{CdCl}_2 + 7\text{H}_2\text{O}$ ;  $\text{NH}_4\text{Cl}, \text{MgCl}_2 + 6\text{H}_2\text{O}$ ;  $\text{KCl}, \text{MgCl}_2 + 6\text{H}_2\text{O}$ , and of the double bromides  $\text{BaBr}_2, \text{CdBr}_2 + 4\text{H}_2\text{O}$ ;  $\text{KBr}, \text{CdBr}_2 + \frac{1}{2}\text{H}_2\text{O}$ ;  $2\text{NaBr}, 3\text{CdBr}_2 + 6\text{H}_2\text{O}$ , and  $3\text{NH}_4\text{Br}, \text{ZnBr}_2$ . The results obtained are similar in character to those of Jones and Ota (*loc. cit.*), and confirm their conclusion that the double salts exist as such to a considerable extent in the more concentrated solutions and are broken down completely by water only in very dilute solution. In the present paper, however, the evidence is made more complete by taking into account the influence exercised by one of the constituent chlorides on the dissociation of the other; it is shown that a solution of a mixture of potassium and ammonium chlorides, in molecular proportion, has a smaller conductivity than the sum of the conductivities of the two salts, although, as is well known, a double chloride is not formed. But as the differences, due to the prevention of dissociation by the presence of a common ion, between the observed and calculated conductivities of solutions of the mixtures  $\text{KCl}, \text{NH}_4\text{Cl}$  and  $\text{KCl}, 2\text{NH}_4\text{Cl}$  are much smaller than those observed in the case of the double chlorides studied, the conclusion reached by Jones and Ota is regarded as justified.

Attempts to obtain evidence as to the condition of the halogen double salts in aqueous solution from the molecular depression of

the freezing point gave abnormal results, which will be dealt with more fully later.

The following salts are new: *sodium cadmium bromide*,  $2\text{NaBr} \cdot 3\text{CdBr}_2 + 6\text{H}_2\text{O}$ , forms beautiful plates; *zinc ammonium bromide*,  $3\text{NH}_4\text{Br} \cdot \text{ZnBr}_2$ , crystallises from a solution containing the constituent salts in the proportion required to form the salt  $2\text{NH}_4\text{Br} \cdot \text{ZnBr}_2$ . W. A. D.

**Electrolytic Behaviour of Platinic and Stannic Chlorides.** By W. DITTENBERGER and RUDOLF DIETZ (*Ann. Phys. Chem.*, 1899, [ii], 68, 853—859).—Kohlrausch (Abstr., 1898, ii, 203) and Hittorf and Salkowski (this vol., ii, 398) have shown that, in the electrolysis of platinic chloride solutions, the platinum is present in the anion, and that any deposition of the metal at the cathode is due to secondary reactions. The authors have determined the transference ratios in the case of solutions of platinic chloride and of hydrogen platinochloride; the values indicate a decrease, with concentration, of the transference ratio of the anion. The conductivity of solutions of platinic chloride increases with time, but this is not due to decomposition into hydrogen chloride and a salt poorer in platinum, as the transference ratios remain unchanged. The agreement of the values of these ratios with those obtained for hydrogen platinochloride at equal concentration show that probably the latter salt is formed in the solution as represented by the equation  $2\text{H}_2\text{PtCl}_4\text{O} = \text{H}_2\text{PtCl}_6 + \text{PtCl}_2\text{O} + \text{H}_2\text{O}$  (Wagner, this vol., ii, 275). In the electrolysis of stannic chloride, some tin is deposited at the cathode, but this is due to secondary reactions, and it is improbable that decomposition into Sn and Cl ions takes place.

L. M. J.

**Physico-chemical Investigation of the Uranyl Salts.** By CURT DITTRICH (*Zeit. physikal. Chem.*, 1899, 29, 449—490).—The conductivity of a number of uranyl salts of inorganic and organic acids has been determined. The difference between  $\mu_{32}$  and  $\mu_{1024}$  for uranyl chloride, nitrate, and sulphate is abnormally high, probably because the dissociation takes place in stages. The conductivity of the uranyl salt solutions increased appreciably when they were left for some time: thus hydrolysis takes place readily; the presence of  $\text{H}^+$  ions in the solutions was shown by the inversion of sugar, and the extent of hydrolysis was determined. Some uranyl salts (especially the oxalate) are very sensitive to light, and the corresponding decomposition was traced in the diminished conductivity. When the conductivities of uranyl salts for the same concentration are compared, it is seen that the conductivity increases with the strength of the acid, and is thus a constitutive property. The migration velocity of the uranyl ion is calculated to be 56 at  $25^\circ$ . Freezing point determinations showed that uranyl nitrate and chloride are dissociated in dilute solution to the extent of 90—95 per cent.; the sulphate is much less dissociated.

Solutions of various uranyl salts were mixed with solutions of the corresponding sodium salts, and both the conductivity and the freezing point depression were determined. The values obtained were in both cases less than those calculated, pointing to a decrease in the

number of ions ; this holds only for salts of weak acids, so that with these uranium has a decided tendency to form complex compounds. This view is supported by the observation that the specific conductivities of the mixed sodium and uranyl salts are in most cases less than those of the sodium salts themselves : in the case of the oxalate, tartrate, and citrate, the specific conductivity of the mixture decreases with increasing concentration of the uranyl salt. From the concentrations at which the specific conductivity is a minimum, conclusions are drawn as to the nature of the complex ion formed. In mixed solutions of the sodium and uranyl salts of weak acids, the formation of a complex ion may be confirmed by migration experiments. Whilst in a mixed solution of uranyl and sodium oxalates the uranium is transported to the anode, it goes to the cathode in a mixed solution of uranyl and sodium chlorides. The direction seems to depend also on the concentration. The solubility of uranyl oxalate is increased by the addition of sodium oxalate—a further proof that a complex ion is formed.

The mixture of uranyl nitrate with sodium salts of organic acids is in most cases accompanied by an absorption of heat. J. C. P.

**Effect of Low Temperatures on Steel.** By FLORIS OSMOND (*Compt. rend.*, 1899, 128, 1395—1398. Compare Abstr., 1894, ii, 283, and Dewar and Fleming, 1896, ii, 4).—The temperature at which iron is transformed from the magnetic to the non-magnetic state is lowered by the addition of nickel, manganese, or carbon, either separately or collectively, and specimens of steel may be obtained, having at ordinary temperatures the same properties that iron has above 860°. The transformation, however, is always possible at lower temperatures, and the author's experiments indicate that certain nickel and manganese steels, when cooled in liquid air, become magnetic ; at the same time, their specific gravity is diminished. The magnetic condition when once induced persists at high temperatures. When the proportion of the foreign element is further increased, as, for example, in a steel containing 13 per cent. of manganese, it is found that the magnetic condition is not attained even at the temperature of liquid air. The lowering of the transformation temperature of iron by the addition of other elements seems to be comparable with the lowering of the freezing point of a solvent by the increase in concentration of the dissolved substance. G. T. M.

**Thermal Deformation of Crystallised Sulphates of Potassium, Rubidium and Cæsium.** By ALFRED E. TUTTON (*Zeit. Kryst. Min.*, 1899, 31, 426—457 ; *Phil. Trans.*, 1899, 192, A, 455—498).—With the aid of the compensated interference dilatometer (*Phil. Trans.*, 1898, 191, A, 313), determinations have been made of the thermal expansion in the three axial directions of the orthorhombic crystals of the normal sulphates of potassium, rubidium and cæsium. Like the other physical properties, they are functions of the atomic weights of the metals.

The constant  $\alpha$  (coefficient of linear expansion at 0°).

Axis.	K <sub>2</sub> SO <sub>4</sub> .	Rb <sub>2</sub> SO <sub>4</sub> .	Cs <sub>2</sub> SO <sub>4</sub> .
<i>a</i>	0·000 036 16	0·000 036 37	0·000 033 85
<i>b</i>	0·000 032 25	0·000 032 14	0·000 031 95
<i>c</i>	0·000 036 34	0·000 034 63	0·000 035 90
Total (coeff. of cubical expn. at 0°).	0·000 104 75	0·000 103 14	0·000 101 70

The constant  $b$  (half the increment of the linear coefficient per degree of temperature).

Axis.	$K_2SO_4$ .	$Rb_2SO_4$ .	$Cs_2SO_4$ .
$a$	0·000 000 0144	0·000 000 0203	0·000 000 0214
$b$	0·000 000 0141	0·000 000 0184	0·000 000 0182
$c$	0·000 000 0413	0·000 000 0380	0·000 000 0414
Total (half the increment of cubical expn. per degree of temp.)	0·000 000 0698	0·000 000 0767	0·000 000 0810

The coefficients of cubical expansion exhibit a progression corresponding with the progression of the atomic weights of the three respective metals. This is true of both the constants  $a$  and  $b$  in the general expression for the coefficient of cubical expansion,  $\alpha = a + 2bt$ , for any temperature  $t$ . The order of progression of the two constants is inverted;  $a$  diminishes with increasing atomic weight of the metal, while  $b$  increases. Consequently, the coefficients of cubical expansion of the three salts converge with rise of temperature, until they attain equality at about  $136^\circ$ ; beyond this temperature, divergence occurs, and an increase of atomic weight is now accompanied by an increase of expansion.

In the potassium and caesium salts, the maximum thermal axis is the crystallographic axis  $c$ , whilst in the rubidium salt it is  $a$ ; but at  $50^\circ$  rubidium sulphate becomes thermally uniaxial, and above this temperature the maximum thermal axis is the axis  $c$ . As a consequence of this reversal, which is analogous to that shown by the optical characters, the coefficients of linear expansion for any one direction of the three salts do not exhibit any progression corresponding with that of the atomic weights.

L. J. S.

**Thermochemistry of some Opium Alkaloids.** By ÉMILE LEROY (*Compt. rend.*, 1899, 129, 220—223).—The following table gives in Cals. the heats of combustion, formation, and combination with hydrogen chloride of codeine, thebaine, papaverine, and narcotine.

	Combustion.		Formation.	Combination with gaseous HCl.
	At const. vol.	At const. press.		
Codeine .....	2325·8	2327·7	+92·2	+29·74
Thebaine .....	2439·9	2441·8	+74·6	+24·31
Papaverine .....	2477·2	2478·8	+131·9	+26·48
Narcotine .....	2643·8	2644·8	+223·5	+21·72

The heats of neutralisation of the solid alkaloids by dilute hydrochloric acid are: codeine, +9·27 Cal.; thebaine, +6·93 Cal.; papaverine, +4·15 Cal.; narcotine, +2·33 Cal.

The heat of hydration of codeine is +2·23 Cal. (liquid  $H_2O$ ) and +0·67 Cal. (solid  $H_2O$ ); the heat of dissolution of the hydrate is



-0.68 Cal. The heat of dissolution of hydrated codeine hydrochloride is -7.79 Cal. at about 17°, and its heat of hydration is +4.72 Cal. (liquid water) and +1.60 Cal. (solid water).

The heat of dissolution of hydrated thebaine hydrochloride is -5.21 Cal. at about 20°, and its heat of hydration +5.23 Cal. (liquid H<sub>2</sub>O) and +3.67 Cal. (solid H<sub>2</sub>O).

The change of the oily precipitate of papaverine into a crystallised precipitate develops +1.26 Cal. The heat of dissolution of papaverine hydrochloride is -4.93 Cal. at about 18°.

The heat of dissolution of anhydrous narcotine hydrochloride is -1.99 Cal. at about 18°.

The heat of neutralisation of solid morphine by dilute hydrochloric acid being +7.18 Cal., and by gaseous hydrogen chloride +27.97 Cal. (this vol., ii, 465), the energy of the basic function of the alkaloids decreases in the following order: codeine, morphine, thebaine, papaverine, narcotine.

C. H. B.

**Minimum Boiling Points and Vapour Compositions.** By J. H. PETTIT (*J. Physical Chem.*, 1899, 3, 349—363).—Bancroft has shown that it is probable that "consolute liquids with intersecting vapour pressure curves form solutions for which a maximum or minimum vapour pressure exists at some concentration." The author finds that the boiling point curves of mixtures of chloroform or acetone with methylic alcohol have minima at a concentration of about 90 per cent. of the alcohol, and reviews the similar cases at present known. In all, sixteen cases of minimum boiling points in liquids have been observed, and in ten of these the vapour pressure curves intersect, but in the remainder, vapour pressure data are not available. The composition of the vapour phase in equilibrium with the liquid was determined for mixtures of methylic alcohol and acetone, the method employed being the determination of the boiling point of small quantities distilled over between narrow limits of temperature. The vapour curve lies above that of the liquid throughout, except at the minimum boiling point, so that for any mixture of the two constituents this constant mixture must distil over first, and either alcohol or acetone remain in the flask; contrary to the statements of Otto (*Bull. Soc. Chim.*, 1894, [iii], 11, 199) and Monnet (*ibid.*, 1895, [iii], 13, 113), at no concentration can pure acetone pass over first by any method of distillation.

L. M. J.

**Some Boiling Point Curves.** By JOHN K. HAYWOOD (*J. Physical Chem.*, 1899, 3, 317—327).—The boiling points of mixtures of several organic liquids have been determined and the corresponding curves drawn; these show, in many cases, a maximum or minimum point. The closeness of the boiling points of the two constituents seems favourable to the existence of a maximum or minimum point, although a mixture of chloroform and carbon tetrachloride is an exception. In general, one constituent remaining the same, chemically similar substances have similar boiling point curves. A mixture, however, of acetone and chloroform shows a maximum point, whilst one of acetone and carbon tetrachloride shows a minimum point, the curves being quite dissimilar.

J. C. P.

**Relationship between the Melting Points of Organic Substances and the Number of Carbon Atoms in the Molecule.** By WASSILY SOLOVINA (*Chem. Centr.*, 1899, i, 327—328; from *J. Russ. Chem. Soc.*, 1898, 30, 819—822).—Monobasic saturated fatty acids with an even number of carbon atoms have a higher melting point than those with an uneven number in the series immediately preceding or following. The amides of these acids and of dibasic saturated fatty acids show the same regularity, also the normal saturated diamines, and the corresponding dibromides and diphenylic ethers. Compounds of other than normal structure do not show this regularity. In the case of the substituted malonic acids, the compounds with an uneven number of carbon atoms have the higher melting point; in that of the substituted succinic acids, increase in the number of carbon atoms is accompanied by a fall in the melting point. J. C. P.

**Vapour Pressure of Solutions of Volatile Substances.** By R. A. LEHFELDT (*Zeit. physikal. Chem.*, 1899, 29, 498—500).—When a small quantity of a volatile liquid A is dissolved in a volatile liquid B, an equation deduced by Nernst takes the form  $p/\pi_B = (1 - \xi)/(1 - \eta)$ , where  $p$  is the vapour pressure of the solution,  $\pi_B$  that of the solvent B;  $\xi$  is the molecular ratio of A to B in the liquid,  $\eta$  the molecular ratio of A to B in the vapour. For a dilute solution of B in A,  $p/\pi_A = \xi/\eta$ , where  $\pi_A$  is the vapour pressure of the solvent A.

For a solution of tetrachloromethane in toluene,  $\xi$  was calculated to be 0.072, and found to be 0.073; for toluene in tetrachloromethane,  $\xi$  was calculated to be 0.680, and found to be 0.708. For solutions of tetrachloromethane in benzene, and benzene in tetrachloromethane, a good agreement was found between the observed and calculated values of  $\xi$ . Mixtures containing alcohol have maximum vapour pressures, and even for dilute solutions the deviations from the formulæ are considerable. For a solution of alcohol in benzene,  $\xi$  was calculated to be 0.070, and found to be 0.088. J. C. P.

**Thermal Properties of Isopentane.** By SYDNEY YOUNG (*Zeit. physikal. Chem.*, 1899, 29, 193—241).—The purity of the samples of isopentane employed was proved by the constancy of the boiling point, the density, critical temperature, and pressure, and by the agreement between the values of the vapour pressure obtained by the statical and dynamical methods. The boiling point was 27.95° at 760 mm., a value somewhat lower than that generally accepted, and the critical temperature and pressure were found to be 187.8° and 25,015 mm., values in good accord with previous observations. The vapour pressures were determined at temperatures from -31° to the critical point by the method previously described (*Trans.*, 1889, 55, 483), and the results are in good accord with those calculated by the formula  $\log. p = a + ba^t + c\beta^t$ . The orthobaric volumes were determined by both direct and indirect methods (Thomas and Young, *Trans.*, 1893, 63, 1191), and complete tables are given for the volume of 1 gram of liquid, of vapour, and of liquid and unsaturated vapour. In measuring pressure, it was found that mercury vapour does not reach its maximum pressure for some time, and the pressure due to it is uncertain, but no appreciable error was introduced thereby.

The mean density of liquid and saturated vapour is given by the formula  $D = 0.3197 - 0.000454t$ . From the data found, tables of the isobars are obtained for pressures varying from 4000 to 56,000 mm. and for temperatures from  $10^{\circ}$  to  $220^{\circ}$ , and of the isochors for volumes ranging from 1.58 c.c. to 4000 c.c. From these, the values of  $dp/dt$  can be readily obtained for various volumes ( $=b$  in equation  $p = bT + a$ ); they are found to increase with rise of temperature when the volume is below the critical volume, but to decrease above, except for large volumes when the values are constant; the variations are too regular to be ascribed to experimental errors. At higher temperatures, the values of the expression  $1000/bv$  reaches a constant value of 11.36 at a volume of 200 c.c., the value calculated from the molecular weight being 11.6. The values of  $a$  in the equation  $p = bT + a$  are also given for various volumes. The ratios of the absolute temperature and molecular volumes of liquid and of vapour to the corresponding critical constants are found to be almost identical with those of benzene at 'corresponding' pressures, as are also the ratios of the actual to the theoretical vapour density, so that liquid isopentane, like benzene, consists of simple molecules (see Rose-Innes, *Abstr.*, 1897, ii, 542).

L. M. J.

**Cryohydrates.** By A. PONSOT (*Compt. rend.*, 1899, 129, 98—100).—The temperature and composition of a cryohydric bath depend on the degree of purity of the salt. With a pure salt, the temperature is remarkably constant; if, however, an impure salt is employed, the temperature is not constant during solidification, the amount of variation depending on the degree of impurity, on the fraction of the solution which has solidified, and on the rate of cooling. If the vessel containing the cryohydric mixture is in direct contact with the freezing mixture, the temperature of the liquid portion is not always independent of that of the freezing mixture or of the rate of stirring. This is due to the fact that the rate of solidification of the salt does not increase so much as that of the ice in the freezing mixture, and so the cryohydric mixture becomes more and more concentrated.

H. R. LE S.

**Cryoscopic Behaviour of Alcohols.** By WILHELM BILTZ (*Zeit. physikal. Chem.*, 1899, 29, 249—265).—Cryoscopic observations were made in the case of a large number of alcohols in benzene and naphthalene solutions in order to further verify the conclusions previously arrived at (this vol., i, 297). The effect of molecular weight was determined by the examination of eight primary alcohols, from normal propylic to cetylic alcohol. Curves constructed for concentration against percentage difference from normal molecular weight show that in all cases the abnormality increases with concentration but to a less degree the higher the molecular weight. For determinations of constitution, therefore, the curves of compounds of approximately equal molecular weights should be compared. Eighteen secondary and tertiary alcohols were next examined and the curves for molecular weight against depression are compared with those of the primary alcohols of equal molecular weight. The general results previously found are verified, the secondary alcohols being less abnormal than

the primary, but more so than the tertiary, the differences being more marked the greater the molecular weight; unsaturated alcohols give a steeper curve than the corresponding saturated compound. Ramsay and Shields have shown that the association in alcohols decreases with increasing molecular weight (*Trans.*, 1893, 1089), a conclusion also reached by Traube (*Abstr.*, 1896, ii, 411) and in accord with the results just described.

L. M. J.

**Modification of van der Waal's Equation.** By LUDWIG BOLTZMANN and H. MACHE (*Ann. Phys. Chem.*, 1899, [ii], 68, 350—351).—As a modification of van der Waal's expression, the authors propose the equation  $(pT + a/v)(v - 1/3b) = rT(v + 2/3b)$ , and show that this gives values for the pressure of carbonic anhydride at various volumes and temperatures in accord with Amagat's observations. The agreement is by no means complete, but they state that it is closer than that obtained with van der Waal's expression, and suggest that better agreement would probably be obtained in the case of the more permanent gases, such as hydrogen, argon, &c.

L. M. J.

**Limits of the Solid State. III.** By GUSTAV TAMMANN (*Ann. Phys. Chem.*, 1899, [ii], 68, 553—583; 629—657).—The paper contains an account of a large number of determinations of the effect of pressure on the melting or a transition point, the method being the determination of the pressure during fusion or a transition, when the substance was maintained at a constant temperature, the manometric reading having been previously verified. Where data for comparison are available, the results appear to agree well with those of other observers. The pressures are expressed throughout in kilograms per sq. cm. The compounds examined were naphthalene, water, carbonic anhydride, ethylenic bromide, hydrogen cyanide, hydrated calcium chloride,  $\text{CaCl}_2 + 6\text{H}_2\text{O}$ , methylthiocarbimide, paraxylene, diethylamine, dimethylethylcarbinol, trimethylcarbinol, acetic acid, sulphur, sodium, mercury, machine oil, hexachlorethane, ammonium nitrate, and silver iodide. In all cases, the curves are concave to the pressure axis as long as the latent heat of fusion or transition is positive except in a few cases of anomalous specific heats. By extrapolation of the curves, which are of the form  $t = t_0 + ap - bp^2$ , maximum melting temperatures are indicated at the temperature and pressure corresponding with  $p = a/2b$ , in some cases the maximum was actually obtained. In certain cases, triple points occur where the liquid is equilibrium with two different modifications; from these points, two melting point curves branch, and also a transition curve giving the temperatures and pressures at which the modifications change in the solid state. For naphthalene, the melting point curve was determined from  $t = 80^\circ$ ,  $p = 1$  to  $t = 190^\circ$ ,  $p = 3600$ , the maximum being indicated at  $261^\circ$  and  $p = 11,500$ . The values of  $dT/dp$  at atmospheric pressure is  $0.0366$ , that calculated from the specific volumes and latent heat of fusion being  $0.0439^\circ$ . For water, very interesting results were found, the pressure at  $-40^\circ$  being less than at  $-39^\circ$ , so that at some temperature between  $-35^\circ$  and  $-40^\circ$  the value  $dT/dp$  becomes infinite and hence the latent heat of fusion is zero. By further cooling, if the curve is continuous, a lower temperature should be reached at which ice at

atmospheric pressure would melt to an amorphous, viscid liquid. The specific volumes of ice and water do not become zero with the specific heat, the difference still being at least 2 per cent. With carbonic anhydride, a triple point occurs at  $t = -7.5^\circ$ ,  $p = 2800$ , and the equations for the three curves meeting at this point were obtained. At the critical temperature of the gas, the melting point pressures of the two modifications are respectively 6070 and 4200, the transition pressure being 6500. Ethylenic bromide gave a normal curve with maximum indicated at  $178^\circ$  and  $p = 12,900$ , but above  $80^\circ$  a change into a second modification occurs, and the values obtained during cooling are lower than the previous set, and apparently indicate two curves cutting at about  $60^\circ$ . Hydrogen cyanide, examined at temperatures up to  $50.9^\circ$ , gave a curve represented by  $t = 13.4 + 0.02187 p - 0.0_5 1475 p^2$  with a maximum at  $81^\circ$ ; calcium chloride, with  $6H_2O$ , gave results in accord with  $t = 29.7 + 0.01163 p - 0.0_6 6 p^2$ , a maximum is indicated at  $86^\circ$ , and the measurements were carried to  $60.2^\circ$ . Dimethylethylcarbinol was examined at temperatures up to  $34^\circ$ , and the results are represented by  $t = -9.0 + 0.01833 p - 0.0_8 193 p^2$ ; maximum  $= 36.5^\circ$ . With paraxylene, two curves were obtained for two modifications which at atmospheric pressure melt at  $12.6^\circ$  and  $15^\circ$  respectively. Diethylamine yields a curve consisting of two parts meeting at about  $-20^\circ$ . Just beyond the triple point the value of  $dT/dp$  in one curve tends to become infinite, and hence the latent heat zero, whilst in the other it tends to zero, and hence the specific volumes of solid and liquid become equal. The melting point curve of trimethylcarbinol has a triple point at  $60^\circ$  and 1700; for acetic acid, the curve is given by  $t = 16.6 + 0.0220 p - 0.0_5 24 p^2$ , and hence has a maximum at  $p = 4600$ , but a triple point is reached at 1900 kilos. and  $44^\circ$ . The melting point curve of the rhombic variety of sulphur was determined to a pressure of over 3000, and temperature of  $190^\circ$ ; the transition curve of rhombic and monoclinic varieties was determined from  $95^\circ$  to the triple point at  $150^\circ$ , and the melting point curve of the monoclinic variety at temperatures below this was also found. The value of  $dT/dp$  at ordinary pressure was found to be 0.0294, that calculated being 0.0266. The melting point of sodium was found to increase to  $120.3^\circ$  at 2840 kilos. the value of  $dT/dp$  being 0.0077 (calculated 0.0068). Observations with mercury gave the value  $-27.2^\circ$  at 2138 kilos., giving  $dT/dp = 0.0054$ , the calculated value being 0.00507. Ammonium nitrate melts at  $161^\circ$ , and below this temperature forms a second modification at  $125.6^\circ$ , undergoing a third transition at  $82.8^\circ$ , whilst at  $32.4^\circ$  a fourth modification occurs. Below  $100^\circ$  therefore, three transition curves are possible and were traced; they meet in a triple point at  $64.16^\circ$ ; the transition curve of the second to the third modification, starting at  $84.6^\circ$ , has a negative value for  $dT/dp$  corresponding with a negative value for the volume change during transition. Doubly refractive silver iodide changes at  $145^\circ$  to the regular form, and the transition curve was determined; this, like that for water, is a descending curve to about  $100^\circ$ , but between this temperature and  $90^\circ$  a discontinuity occurs, and in the portion below  $90^\circ$  the interesting case of an infinite value for  $dT/dp$  is reached, so that the latent heat is zero. The author then discusses the probable general form of the melting point curve.

Poynting's supposition that it is similar to the vapour pressure curve is not supported, and the assumption that the volume change and latent heat vanish together is erroneous. The author further considers that no gradual change from crystalline to liquid condition can occur, and that the form of the curve is not in accord with the idea of a crystal. The general form is probably that of a closed curve, and this is especially indicated by the curves of water, diethylamine, and silver iodide.

L. M. J.

**Crystalline Liquids.** By RUDOLF SCHENCK and FR. SCHNEIDER (*Zeit. physikal. Chem.*, 1899, 29, 546—557. Compare Schenck, *Abstr.*, 1898, ii, 286, 563; this vol., ii, 360).—1:4-Azoxyanisole melts at 116.8° to a cloudy, crystalline liquid, becoming an ordinary isotropic liquid at 134°. The process is reversible and the two modifications are enantiotropic, that is, the vapour pressure curve of the liquid cuts the vapour pressure curves of the two crystalline modifications above the point of intersection of the latter. When benzophenone is dissolved in the azoxyanisole, the temperature at which the isotropic liquid becomes crystalline is lowered until it lies below that at which the two crystalline modifications exist together: the enantiotropic modifications therefore are now monotropic. The quadruple point at which vapour, solid crystalline substance, and the solutions of benzophenone in the isotropic and crystalline liquids exist together is 114.9°.

It has been shown that 1:4-azoxyanisole and 1:4-azoxyphenetole in the liquid crystalline condition form an isomorphous mixture. When, however, a solution of the latter in the former is cooled, pure solid azoxyanisole separates out, and the depression of the solidifying point is proportional to the concentration of azoxyphenetole. The heat of solidification is thus calculated to be 31.2 Cal.; calorimetric determination gives 29.84 Cal., and Hulett previously found the value 29 Cal.

The temperature at which liquid crystals of 1:4-azoxyanisole separate from the isotropic liquid is lowered by the addition of other substances. The author tests by a number of experiments how far this may be made the basis of a molecular weight determination. In this and similar cases, it seems that the liquid crystals do not separate out in the pure state.

J. C. P.

**Gaseous Reactions in Chemical Kinetics. II. Influence of Temperature on the Formation and Decomposition of Hydrogen Iodide.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 29, 295—314).—The variation of chemical equilibrium with temperature is given by the expression  $d \log. k/dT = q/RT^2$  where  $q$  is the heat development of the reaction; if  $q$  is constant therefore, its value may be deduced by the expression obtained from the integration of the above equation  $q = R(\log. K_2 - \log. K_1) \cdot T_1 T_2 / (T_2 - T_1)$ . As  $q$ , however, usually is a function of the temperature, this expression can be applied only for two temperatures not far removed, but by a number of such determinations the values of  $q$  for various mean temperatures can be obtained. In the case of the decomposition of hydrogen iodide, the author finds the expression  $q = A + BT + CT^2$  and hence  $\log. K = -A/RT + B \log. T/R + CT/R + \text{constant}$ , and experiments show that the found values

of  $K$  agree well with those calculated for temperatures from  $280^\circ$  to  $520^\circ$ . The value of  $K$  is, however, the ratio of the velocity constants of the decomposition and formation, so that  $\log. K = \log. k_1 - \log. k_2$  and hence  $\log. k_1$  and  $\log. k_2$  must be both expressed as temperature functions similar in form to that of  $\log. K$ , that is,  $\log. k_1 = -a_1/T + b_1 \log. T + c_1 T$  and  $\log. k_2 = -a_2/T + b_2 \log. T + c_2 T$ , &c., where  $a_1 - a_2 = A/R$ ,  $b_1 - b_2 = B/R$ , and  $c_1 - c_2 = C/R$ . The values of the velocity constant for the decomposition are found and the values of the constants  $a_1$ ,  $b_1$ ,  $c_1$ , obtained; the calculated and found values agree well throughout the whole range of temperature. The velocity constants for the formation were next found, and the values are compared with those deduced from the formula  $\log. k_2 = -(a_1 - A/R)/T + (b_1 - B/R) \log. T + (c_1 - C/R)T$ , the agreement being closer than would be expected for experimental work of this nature. The value for the heat of formation of hydrogen iodide obtained by the author's formula does not agree with that found by Thomsen at  $20^\circ$ ; not only are the calorimetric observations uncertain, however, but little reliance can be placed on values obtained by the extrapolation of  $260^\circ$ . The ratios of the velocity constants for a difference of  $10^\circ$  increase from 1.5/1 at  $500^\circ$  to 1.8/1 at  $300^\circ$ , values which, as would be expected, are somewhat less than those obtained for reactions at ordinary temperatures (this vol., ii, 548).

L. M. J.

**Gaseous Reactions in Chemical Kinetics. III. Formation of Hydrogen Sulphide from its Elements.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 29, 315—333).—The velocity of formation of hydrogen sulphide from the elements was determined at temperatures of  $356^\circ$ ,  $310^\circ$ ,  $283^\circ$ , and  $234^\circ$ , and the results are in good accord with those calculated for a reaction of the first order, the sulphur concentration being constant during each experiment. The values for the velocity constants were  $k_{356} = 0.0028$ ,  $k_{310} = 0.000118$ ,  $k_{283} = 0.0000329$ , and  $k_{234} = 0.0000018$ . The reaction is hence perfectly normal in its course, and the "limit of formation" and "false equilibrium" observed by Pélabon are not verified (Abstr., 1897, ii, 312). Since the reaction is of the first order with respect to the hydrogen, it must be represented by the equation  $H_2 + S = SH_2$ . With varying sulphur concentration, the velocity was found to be proportional to the square root of the concentration, a surprising result in view of the complexity of sulphur molecules. It may, however, be explained by the assumption that three actions occur—(I)  $S_8 \rightleftharpoons 4S_2$ , (II)  $S_2 \rightleftharpoons 2S$ , (III)  $H_2 + S = SH_2$ , and that of these the velocity of I is very small, and of II very great compared with III. The velocity of III will then be proportional to the square root of the concentration of the  $S_2$  molecules, and this, owing to the rapid removal of the latter, proportional to the concentration of the  $S_8$  molecules. The results are also verified by the comparison of the first set of experiments with constant sulphur concentration with the second set, in which it was variable; the agreement is satisfactory. The ratio of the velocity constants for a difference of  $10^\circ$  increases from 1.39/1 at  $234^\circ$  to 1.77/1 at  $356^\circ$ ; such an increase with rise of temperature is very exceptional, but is, in this case, explicable, as, owing to the various molecular groups, an unknown proportionality factor between

the active mass of the sulphur and the actual concentration exists, this factor probably increasing with rise in temperature. L. M. J.

**Gaseous Reactions in Chemical Kinetics. IV. Formation and Decomposition of Hydrogen Selenide.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 29, 429—448).—Hydrogen selenide differs from hydrogen sulphide in the fact that its formation and decomposition take place under the same conditions. According to Pélabon (*Abstr.*, 1897, ii, 251), true equilibrium is established only above 320°; below this temperature, both formation and decomposition stop short of the point of equilibrium.

Above 320°, the author finds that the union of hydrogen and selenium is much more rapid than in Pélabon's experiments, and shows that the acceleration is due to the catalytic action of a selenium deposit inside the bulbs; the velocity constant is proportional to the ratio: selenium surface/volume of bulb. The decomposition of hydrogen selenide proceeds slowly until selenium is deposited, whilst the reaction is rapid from the first, when free selenium is present.

The equation expressing the progress of the reaction is  $dx/dt = k(a-x) - k_1x$ , where  $a$  is the initial concentration of the hydrogen. Kistiakowsky's integration of this gives  $k = \xi/t \cdot \log. \xi/(\xi - x)$ , where  $\xi$  is the maximum value of  $x$  at the point of equilibrium, and the initial concentration of the hydrogen is 1; a similar equation can be obtained for  $k_1$ . When half the bulb was coated with selenium,  $k = 0.000119$ : when it was completely coated,  $k = 0.000251$ , whilst an increase in the surface relatively to the volume of the bulb raised the value of  $k$  to 0.000527. A comparison of the values of  $k_1$ , (1) when no free selenium is present, (2) when free selenium is present from the first, shows that the non-catalytic decomposition of hydrogen selenide is at least ten times slower than that at the selenium surface.

This catalytic acceleration of the reaction has enabled the author to show that, even below 320°, true points of equilibrium can be reached, as the following table shows:

Temperature.	$\xi$ from formation.	$\xi$ from decomposition.
254°	0.1388	0.1391
274	0.1692	0.1701
301	0.2052	0.2046

It thus appears that the times allowed by Pélabon for his experiments were too short. Above 320° also, the author finds values of  $\xi$  which differ from those of Pélabon, and the point of equilibrium varies with the temperature quite differently in the two cases. Pélabon found that hydrogen selenide had a minimum dissociation at 570°; the author criticises the numbers on which this conclusion rests, and points out an error in Pélabon's formulæ. J. C. P.

**Stability of the Halogen Derivatives of Benzene.** By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1899, 29, 401—422).—Chlorobenzene, bromobenzene, or iodobenzene was added to a solution of sodium in amyl alcohol, and the mixture kept, with the help of a thermostat, at 125°. The amount of halogen eliminated was



determined from time to time by titration. The velocity of reaction for iodobenzene, calculated from the formula  $k = 1/t \cdot \log. a/(a-x)$ , varied from  $2.09 \times 10^{-4}$  to  $3.82 \times 10^{-4}$ ; this value is about 90 times greater than the corresponding constant for bromobenzene. The presence of air very greatly increases the velocity of reaction, and may account for the large variation of the constant. When a current of air was led through the mixture at  $125^\circ$ ,  $k$  for iodobenzene varied from  $258 \times 10^{-4}$  to  $306 \times 10^{-4}$ , and with a stronger current of air a still larger value was obtained. This difficulty led the author to determine only *relative* velocities of reaction under the same conditions. At  $125^\circ$ , and with a steady current of air passing, bromobenzene was decomposed about 550 times as rapidly as chlorobenzene. At  $50^\circ$ , under similar conditions, the value of  $k$  for iodobenzene is about 310 times that for bromobenzene. The influence of temperature is unexpectedly small; for bromobenzene,  $k = 1.37 \times 10^{-4}$  at  $50^\circ$ , and  $12.6 \times 10^{-4}$  at  $125^\circ$ . This is regarded as probably due to secondary causes.

Two similar solutions of sodium in amylic alcohol, through one of which air was passed for a considerable time, were equally effective, so that the acceleration of the reaction cannot be due to any oxidation products of the amylic alcohol. The influence of air on the reaction was exactly the same when ethylic alcohol was employed instead of amylic alcohol.

J. C. P.

**Internal Friction of Solutions of Ethereal Salts in Supercooled Thymol.** By CARL SCHALL (*Zeit. physikal. Chem.*, 1899, 29, 423—428).—In continuation of the author's work on the internal friction of glycerol solutions (Schall and van Rijn, *Zeit. physikal. Chem.*, 1897, 23, 329), experiments have been made with thymol as a solvent; it is less hygroscopic, more easily obtained pure, and can be kept for some time in a supercooled condition.

When  $t$  is the time of flow,  $s$  the specific gravity, and  $\theta$  the temperature, the equation  $t.s = 23.2 (415 - \theta)/\theta \div 1.0176 \times 150/\theta$  gives values of the product  $t.s$ , agreeing well with those experimentally determined. A slightly modified formula was employed at higher temperatures. Thus  $t.s = f(\theta)$ , and for a solution of an ethereal salt in thymol,  $t_1.s_1 = f(\theta + \Delta)$ , where  $\Delta$  is the depression of the freezing point of the solution; this equation may be used to calculate  $\Delta$ . For a 5.58 per cent. solution of amylic propionate in thymol,  $\Delta$  was found  $= 3.167^\circ$ ; the value calculated from the latent heat of fusion is  $3.29^\circ$ , from the experimentally determined molecular depression  $3.22^\circ$ . A 4.06 per cent. solution of ethylic valerate shows an equally good agreement, but much less satisfactory values of  $\Delta$  are obtained for an ethylic acetate solution, as well as for amylic propionate solutions at higher temperatures.

J. C. P.

**Surface Tension of Aqueous Solutions.** By CARL FORCH (*Ann. Phys. Chem.*, 1899, [ii], 68, 801—816).—The author has determined the surface tension of a number of solutions in order to test the validity of the conclusions arrived at by Traube (*Abstr.*, 1891, 1408). The method employed was that based on the determination of the weight of a drop from a small aperture; this is dependent on the time interval between successive drops, and all weights were corrected by a linear

formula to a time interval of 5 seconds and to  $18^{\circ}$ . Comparison with the results of Quincke and Volkmann indicates the validity of the method, and the molecular depression or elevation of the surface tension was determined for a number of compounds. With sodium sulphate, chloride, and nitrate, phosphoric acid, and cane sugar, it was found that the molecular elevation remains nearly constant to high dilutions, a slight decrease with dilution being observed. For nitric acid and the fatty acids (from formic to nonylic), depression occurs, the surface tension of the solution being less than that of water, and the value of the molecular depression increases greatly with dilution. In the case of valeric and the higher acids, the values reach a maximum, and afterwards decrease, so that a constant value is not attained, a result opposed to the conclusions of Traube. Curves are given for the lowering of surface tension plotted against the cube root of the concentration, and also for the latter against the molecular lowering multiplied by 1, 3,  $3^2$ , &c., as the series from nonylic acid is descended. These curves show the approximate validity of Traube's statement that the entrance of a  $\text{CH}_2$  group increases the molecular cohesion threefold in dilute solutions; the curve for valeric acid is, however, anomalous. The molecular depressions for formic and acetic acids calculated by a formula  $w/m = k + L \cdot \alpha$ , where  $\alpha$  is the degree of dissociation, do not agree with the observations, so that the connection with dissociation is not given by this simple expression. L. M. J.

**Determination of Invasion and Evasion Coefficients in the Solution of Gases in Liquids.—Carbonic Anhydride in Water and Aqueous Salt Solutions.** By CHRISTIAN BOHR (*Ann. Phys. Chem.*, 1899, [ii], 68, 500—525).—The author has previously shown (*Abstr.*, 1898, ii, 211) that the absorption coefficient of a gas between about  $0^{\circ}$  and  $30^{\circ}$  is given by the expression  $a(T - n) = k$ . A saturated solution of a gas may, however, be regarded as a system in equilibrium, in which the velocities with which the gas leaves and enters the solution are equal, and the author has attempted to determine these, which he calls the "evasion" and "invasion" velocities. The absorption coefficient was first determined for carbonic anhydride in water and in aqueous salt solutions. In the latter, also, the form of the absorption coefficient considered as a temperature function was similar to that previously found for water. The value for  $n$  is slightly lower for salt solutions than for pure water, and is not quite constant, but increases slightly with rise of temperature. In the determination of the evasion coefficient, the author first assumes that in any short interval of time the quantity of gas leaving the liquid is proportional to its concentration, that is,  $dx = -b \cdot x \cdot dt$ , where  $x$  is the concentration and  $b$  depends on the evasion coefficient, surface, and volume. This yields  $t = \int_{x_0}^x \frac{dx}{-bx}$  and  $b = (\log. x_0 - \log. x) / t \log. e$ . The validity of the fundamental assumption is proved by the concordance of the values of  $b$  so obtained at different concentrations. The temperature effect was next determined, and it was found that the form of the expression was  $b = 0.00081 (T - 252.7)$ , the values so calculated agreeing well with the determinations. Similar expressions were obtained for the

salt solutions, the values of the evasion being, however, considerably less than for pure water. The values of  $b$  are then corrected for surface, &c., in order to give the absolute evasion coefficient, that is, the number of cubic centimetres of the gas which leaves 1 sq. cm. of the surface per minute when its density in the liquid is 1 c.c. of gas (at  $0^\circ$  and 760 mm.) per c.c. of liquid. If the expression holds for low temperatures, it follows that, at a temperature  $n^\circ$ , no gas would leave the solution.

The invasion coefficient is perfectly analogous to the evasion coefficient, and is similarly defined. It may be determined directly or it may be calculated, being the product of the absorption and the evasion coefficients, since in the saturated solution invasion and evasion are equal. The direct determinations were made by measuring the quantity of gas absorbed per minute when water is exposed to carbonic anhydride at constant pressure, a correction being made for the evasion during the time, inasmuch as the invasion and evasion are assumed to go on independently. The values so obtained agree well with those calculated, as previously stated. In water and the dilute salt solution (68 grams per litre), the values were approximately equal between  $0^\circ$  and  $20^\circ$ , and with the more concentrated solution they were constant to  $40^\circ$ . A connection appears to exist between the invasion ( $\gamma$ ) and the salt concentration, in grams per 100 c.c. ( $C$ ), the form of the equation given being  $\gamma = c - k \sqrt[3]{C^2}$ , from which, by extrapolation, it is found that, at a concentration of 32.95, the invasion coefficient would be zero, but the small number of solutions examined (two and pure water) are hardly sufficient to justify any deductions being drawn. If the invasion coefficient is constant, and the evasion coefficient of the form  $b = k(T - n)$ , it follows that the absorption must, as previously found, be of the form  $a(T - n) = c$ , and the actual values calculated from the two coefficients agree well with the previous determinations.

L. M. J.

**The Affinity between Acids and Bases in Methylic Alcoholic Solution.** By A. MINOZZI (*Gazzetta*, 1899, 29, i, 421—439).—The following table gives the changes in volume produced on mixing equivalent quantities of decinormal acids and bases in methylic alcoholic solution:

	KOH.	NaOH.	MeOK.	MeONa.
HCl.....	6.72	6.47	—	6.57
HBr.....	6.48	6.42	6.48	6.54
CCl <sub>3</sub> ·COOH .....	2.32	2.13	2.22	2.07
CHCl <sub>2</sub> ·COOH.....	2.47	2.31	2.34	2.49
CH <sub>2</sub> Cl·COOH.....	1.66	1.56	1.64	1.68
CH <sub>3</sub> ·COOH .....	1.44	1.40	1.42	1.48

The variation in volume produced by any one acid is sensibly the same for all the bases, showing that, in methylic alcohol, the alkali hydroxides and methoxides act as equally strong bases; this confirms the results of Carrara (*Abstr.*, 1896, ii, 511), who found that, in methylic alcohol, alkali hydroxides and methoxides have nearly the same conductivities.

From the volume alterations observed on mixing solutions of the

different bases with a mixture of hydrochloric acid with one of the acetic acids, the author has calculated the following affinity constants, the numbers in the second column being those found by Ostwald for the same acids in aqueous solution :

	In methylic alcohol.	In water (Ostwald).
HCl .....	100.0	98.0
$\text{CCl}_3 \cdot \text{COOH}$ .....	12.3	80.0
$\text{CHCl}_2 \cdot \text{COOH}$ .....	11.1	33.0
$\text{CH}_2\text{Cl} \cdot \text{COOH}$ .....	7.5	7.0
$\text{CH}_3 \cdot \text{COOH}$ .....	6.3	1.23

Thus, according to the volume-chemical method of measurement, in methylic alcohol hydrochloric acid is about eight times as energetic as trichloroacetic acid ; by the electrolytic method, Carrara (*loc. cit.*) found the ratio of the affinities to be about 30.

T. H. P.

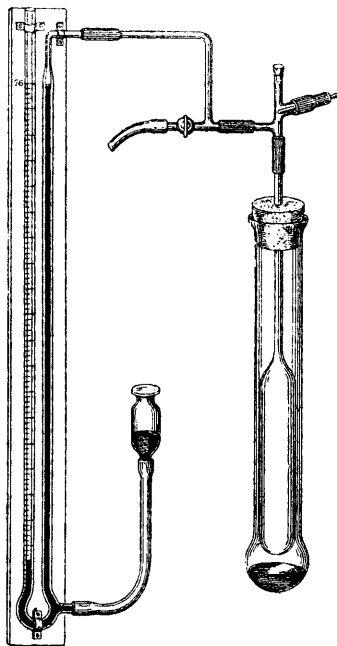
#### Determination of Vapour Density under Arbitrary Pressure.

By OTTO BLEIER and LEOPOLD KOHN (*Monatsh.*, 1899, 20, 505—538).

—The method depends on the determination of the increase of pressure produced by the vaporisation of a known weight of substance in a special form of apparatus. The apparatus consists of (1) a strong bulb of 275 c.c. capacity heated in a Victor Meyer vapour-bath ; (2) a manometer, one limb of which is adjusted to a constant level whilst the other is graduated for reading ; (3) capillary connecting tubes including a tap leading to an air-pump. The capacity of the connecting tubes is only 2 c.c., and the total space outside the vapour jacket only 12 c.c., so that the effect of variations in the atmospheric temperature is negligible.

The molecular weight is determined from a formula of the Beckmann type,  $m = q.c/p$ , where  $q$  is the quantity of substance used,  $p$  the increment of pressure, and  $c$  the "constant of the apparatus." This constant depends on the dimensions of the apparatus and the temperature of the vapour jacket, but if the same bulb, or a bulb of equal volume, is always used, it will only depend on the temperature, and a variation of 3 c.c. in the volume of the bulbs will cause an error in the molecular weight

of only 1 per cent. The constant may be determined in three different ways, (1) by calculation, a correction being introduced for the volume of the apparatus not heated by the vapour-jacket ; (2) by experiment, using a known weight of a pure substance of known molecular weight



or by introducing known volumes of air through the air-pump tap ; (3) by a combination of (1) and (2) determining the constant with a vapour jacket of, say, water, xylene, or aniline, and from this value deducing the constants for other vapour jackets by calculation. Values are given in the paper for the constant of an apparatus of standard size from the boiling point of benzene ( $80^{\circ}$ ) to that of sulphur ( $448^{\circ}$ ), but experiments have not been made at temperatures higher than the boiling point of diphenylamine ( $310^{\circ}$ ).

To secure good results, volatilisation of the substance must be as rapid as possible, and, as a rule, the manometer becomes nearly stationary in about a minute ; the effect of diffusion is to produce a gradual fall of pressure, and the maximum reading is therefore observed, but the error due to diffusion is found to be negligible when the pressure produced by the vapour is not more than three times the initial pressure. For substances boiling at  $40^{\circ}$  above the temperature of the vapour jacket, the initial pressure may be 300 to 100 mm., and the weight of substance up to 0.1 gram ; for substances boiling at  $60^{\circ}$  above the temperature of the vapour jacket, a pressure of 70 to 30 mm. may be used, and a weight of  $1/4$  to  $1/6$  millimol., the results being correct within 1 per cent. ; determinations may also be made with substances boiling  $70$ – $90^{\circ}$  above the temperature of the vapour jacket (as, for example, those which would decompose by further heating), using an initial pressure of 18 to 12 mm. and a weight of about  $1/10$  millimol., the error not being more than 3–4 per cent.

It is claimed for the method that it can be used at much higher temperatures than Hofmann's method for determining vapour densities at reduced pressures, and is at least equally accurate ; that it can be carried out as readily as Victor Meyer's method for determinations at atmospheric pressure, whilst the calculations involved are even simpler ; and that it is well adapted for studying questions of dissociation.

T. M. L.

**Coagulation of Colloidal Solutions.** By J. STARK (*Ann. Phys. Chem.*, 1899, [ii], 68, 618–619).—By the addition of zinc chloride to colloidal solutions of gold, silver, or arsenious sulphide, flocculent precipitates are obtained containing a multitude of minute air-bubbles and resembling those obtained by the precipitation of suspended materials. This supports the view that colloidal solutions consist also of suspended matter in a very fine state of division (Barus and Schneider, *Abstr.*, 1891, 1412).

L. M. J.

**Deliquescence of Potassium, Sodium, and Ammonium Nitrates.** By FREDERICK L. KORTRIGHT (*J. Physical Chem.*, 1899, 3, 328–333).—A salt is deliquescent when the vapour pressure of its saturated solution is less than the partial pressure of the water vapour in the surrounding air. The pressure of the water vapour in the air in which the salt would first deliquesce was determined by using desiccators containing sulphuric acid solutions of known composition and vapour pressure. At  $20^{\circ}$ , ammonium nitrate deliquesces when the vapour pressure in the atmosphere is equal to or greater than 10.8 mm. of mercury ; the corresponding pressures for sodium nitrate and potassium nitrate are 13 mm. and 16 mm. respectively. The latter

values agree well with those calculated on the assumption that the relative lowering of the vapour pressure of a salt solution is proportional to the concentration, and independent of the temperature.

J. C. P.

**Origin of Dalton's Atomic Theory.** By HEINRICH DEBUS (*Zeit. physikal. Chem.*, 1899, 29, 266—294).—A further contribution to the discussion with reference to the origin of Dalton's atomic theory (Abstr., 1898, ii, 67). The author has been unable to find any evidence that Dalton himself stated, in 1810, "that he was led to the atomic theory in Chemistry in the first instance by purely physical considerations," and regards as erroneous the statement of Roscoe and Harden that this was the case ("New View of the Origin of Dalton's Atomic Theory," p. 50).

L. M. J.

**Mendeléeff's Periodic System of the Elements and the New Constituents of the Atmosphere.** By AUGUSTUS PICCINI (*Zeit. anorg. Chem.*, 1899, 19, 295—305; and *Gazzetta*, 1899, 20, 169—181).—The discovery of argon has led to much discussion as to the correctness and usefulness of Mendeléeff's system, but the author considers that the fundamental idea of this classification has been misunderstood.

The suggestion of Rayleigh and Ramsay, that argon should be placed in the eighth group after chlorine, destroys the colligative character of this group, and disturbs the whole classification to a greater extent than Mendeléeff's view that argon may have an atomic weight of 20, and could therefore be placed in the eighth group after fluorine, thus connecting the two small periods.

The position assigned to an element in the periodic arrangement depends, not only on its atomic weight, but on its chemical properties, and the author considers it premature to try to assign places in the system to substances which form no known compound, and have therefore as yet no chemical character. The view that elements exist which have no chemical properties may be correct, and if time shows that argon and other recently discovered gases belong to this class, they cannot find a satisfactory place in Mendeléeff's scheme.

J. C. P.

**The Incandescent Electric Lamp as a Source of Heat in Ether Extractions.** By CYRIL G. HOPKINS (*J. Amer. Chem. Soc.*, 1899, 21, 645—647).—The author uses five 110 volt lamps of 32-candle power for heating an air-bath on which a set of 20 Soxhlet extractors are placed. For perfect safety, it is advisable that the lamps be immersed in water, otherwise the temperature may rise above the igniting point of ether.

J. J. S.

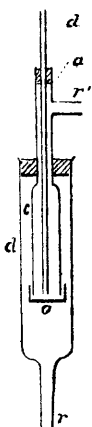
**Vacuum Regulator for Distillations under Reduced Pressure.** By JEAN HAUSSEUR (*Bull. Soc. Chim.*, 1899, [iii], 21, 253—254).—The apparatus described is a simplification of that devised by Auger (this vol., ii, 474). The tube *d* is connected with the pump at *r*, and fitted with a bored stopper, through which a tube *c* is inserted; the latter is fitted at its lower end with a rubber membrane *o*, and is also connected with the pump by the side tube *r'*. The stopper *a* carries a tube *d'*, which is open to the air and can be made to slide up and

down, so that it may be pressed against the membrane *o*. When the pump is working, a partial vacuum is produced on both sides of the membrane, and if the diminution of pressure exceeds a certain limit, depending on the elasticity of the membrane and the position of the tube *d'*, the former is pulled away from the latter and a certain quantity of air is admitted; the pressure in the apparatus is thereby increased and the membrane regains its original position; if the pressure is again diminished sufficiently the process is repeated, and thus the vibratory movement of the diaphragm prevents any considerable alteration of the pressure below a certain limit.

G. T. M.

NOTE.—Neither this apparatus nor Auger's is capable of preventing variations of pressure *above* the limit fixed upon at the commencement of the experiment; such variations may often arise through a falling off of the pump's efficiency.

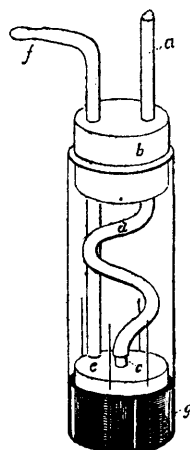
G. T. M.



**Apparatus for Preventing the Backward Flow of Water during Exhaustion with a Water-pump.** By GEORGES CHATANAY (*J. Pharm.*, 1899, [vi], 9, 524—527).—

A small, cylindrical glass bottle about 12 cm. long and 3 cm. wide is interposed between the water-pump and the vessel to be exhausted. This bottle is closed with a cork, *b*, through which two glass tubes pass. The first, a straight tube, *a*, over 760 mm. long, is connected at its upper extremity to the vessel to be exhausted, and its lower end just passes through *b*, and is joined to one end of a piece of thin and narrow indiarubber tubing, *d*, the other end of which is joined to a small piece of glass tubing, *c*, which just passes through a cork, *e*, floating on mercury. It is essential that the length of the tube *c* beyond the lower face of the cork float *e* should not be more than about 1 mm. The second tube which passes through *b* has its upper end connected to the water-pump and the other just reaches to the top of the cork float. Four small rods which pass through the cork float in a vertical direction prevent it from being turned over by any sudden inrush of water. As the cork *e* floats on the mercury the end of the small tube *c* is always below the surface, and an influx of water into the apparatus leads only to a rise of mercury in the long tube *a*.

H. R. LE S.



**Modification of Sprengel's Pyknometer.** By A. MINOZZI (*Gazzetta*, 1899, 29, i, 406—407).—This pyknometer, intended for use with liquids which are volatile or hygroscopic, or which expand rapidly with rise of temperature, consists of a U-tube, one arm of which is a capillary tube drawn out to a point which can be closed by a glass cap, and the other a cylindrical bulb joined to a small stoppered upper

chamber by means of a short capillary tube, on which a mark is scratched at the height to which the instrument is to be filled. If expansion occurs during an experiment, the liquid simply causes it to rise into the small chamber above the bulb. This modification is stated to be more convenient than that devised by Perkin (Trans., 1884, 443) for the same purpose.

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T. H. P.



## Inorganic Chemistry.

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**New Explosive and Detonating Materials.** By UGO ALVISI (*Gazzetta*, 1899, 29, i, 399—405. Compare this vol., ii, 414).—To obtain the maximum effect from an ammonium perchlorate explosive fired by means of a mercury fulminate detonator, the latter must also contain ammonium perchlorate in quantity not greater than 20 per cent. Such mixed detonators are probably the most powerful used, and possess both great disruptive and great propulsive force.

T. H. P.

**Use of Potassium Chlorate in Ammonium Nitrate Explosives.** By HENRI LE CHATELIER (*Compt. rend.*, 1899, 128, 1394—1395).—The addition of potassium chlorate to an ammonium nitrate explosive increases its sensibility to detonators; these two salts form isomorphous mixtures, and the addition is conveniently effected by the use of mixed crystals. Those mixed crystals which contain less than 4 parts of nitrate to 1 of chlorate have the same crystalline form as the latter salt, whilst those containing a greater proportion of nitrate crystallise in forms isomorphous with it. Mixed crystals of definite composition cannot be obtained by evaporating dilute solutions of their constituents to dryness; they are most conveniently produced by dissolving these salts in the mother liquors from previous crystallisations.

G. T. M.

**Action of Chromic Acid on Hydrogen.** By CHARLES L. REESE (*Amer. Chem. J.*, 1899, 22, 158—164).—Ludwig (Abstr., 1872, 590) has stated that when gypsum balls, saturated with aqueous chromic acid, are exposed in an atmosphere of hydrogen, the latter is oxidised; the author now confirms this statement, but points out that in no case is the whole of the hydrogen absorbed. Porous burnt clay balls behave in the same way as those of gypsum, but the absorption is much slower; hydrogen is also absorbed when agitated with chromic acid solution in sealed tubes containing platinised asbestos, although if platinum foil is substituted, no oxidation occurs.

Hydrogen was not oxidised by aqueous chromic acid, either alone or in presence of 1—15 per cent. by volume of concentrated sulphuric acid, at temperatures below 50°, and only very slowly below 100°. After exposure for 116 hours at 100°, 70 per cent. of the gas was oxidised. At 156°, 7 hours exposure led to the oxidation of 11 per cent. of the

hydrogen, a large volume of oxygen being evolved owing to the decomposition of the chromic acid by heat; the oxidation, however, commences at temperatures below those at which oxygen is evolved by chromic acid, and thus does not seem to be dependent on the decomposition of the latter by heat.

Pure chromic acid in aqueous solution is not reduced by the hydrogen evolved on passing an electric current through the solution, but in presence of a trace of sulphuric acid or a sulphate, reduction occurs until a certain limit is reached, apparently dependent on the amount of sulphuric acid present. The behaviour of a solution of potassium dichromate under the influence of an electric current is the same as that of chromic acid.

W. A. D.

**Combination of Carbon Bisulphide with Hydrogen, Nitrogen, [Argon and Carbon Monoxide].** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 133—136).—When a mixture of gaseous carbon bisulphide (70 vols.) and hydrogen (100 vols.) is subjected to the action of the silent electric discharge at an E.M.F. of either 12·6 or 25 volts, both gases partially disappear in the ratio, by volume,  $2\text{CS}_2 : 1\cdot01\text{H}_2$  and a yellow, resinous compound,  $\text{C}_2\text{H}_2\text{S}_4$ , is produced. This has an odour somewhat like that of mercaptan, is insoluble in ether, and but slightly soluble in carbon bisulphide. When a mixture of carbon bisulphide (69 vols.) and nitrogen (100 vols.) is similarly treated, the ratio between the volumes absorbed is  $4\text{CS}_2 : \text{N}_2$  when the current working the coil has an E.M.F. of 12·6 volts, and  $7\text{CS}_2 : \text{N}_2$  with a current of 25 volts; the discharge in the first case lasting for 6 hours, and in the second for 3 hours.

When a mixture of gaseous carbon bisulphide (70 vols.) and argon (100 vols.) is exposed to the silent electric discharge at an E.M.F. of 23·6 volts for 3 hours, the carbon bisulphide disappears together with 2 vols. of argon—the ratio being  $34\text{CS}_2 : \text{A}$ . After 6 hours in another experiment under similar conditions, 3 vols. of argon disappeared, the ratio being  $24\text{CS}_2 : \text{A}$ .

When a mixture of gaseous carbon bisulphide (68 vols.) and carbonic oxide (100 vols.) is subjected to the action of the silent electric discharge for 6 hours, the residual gas measures 3·5 vols. and consists of carbonic oxide free from carbonic anhydride. A yellow substance is formed which is a mixture of the two products obtained when the gases are separately acted on by the silent electric discharge.

H. R. LE S.

**Combination of Nitrogen with Oxygen.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 137—139).—A sample of argon containing nitrogen was purified by mixing it with an excess of oxygen and sparking the mixture over caustic potash. The ratio between the nitrogen and oxygen absorbed was 1·65 in one experiment and 1·84 in another. Now, if all the nitrogen were removed as nitric peroxide, this ratio should be 2, and the caustic potash solution should contain equal amounts of nitrite and nitrate, whereas it was found to contain an excess of the former. These facts are accounted for by supposing that the nitrogen and oxygen first combine to form nitric oxide; this oxide is then oxidised to nitrous anhydride; part of the

nitrous anhydride is further oxidised to nitric peroxide, but some escapes oxidation and dissolves in the solution as such.

H. R. LE S.

[Iodine in Sea Water at Different Depths.] By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 9—15. Compare this vol., ii, 477).—It has been shown previously that the whole of the iodine present in water taken from the surface of the Atlantic Ocean exists either in the form of soluble organic compounds or as part of the substance of infusoria, and it seemed probable that the absence of metallic iodides and iodates is due to the assimilation of these salts by living organisms inhabiting the upper layers of the ocean. To test the validity of this view, an examination was made of samples of water taken from the Mediterranean off Monaco (1) at 0·5 metre below the surface, (2) at a depth of 880 metres, (3) at a depth of 980 metres when the bottom was found. The results obtained are summarised in the following table :

	0·5 m.	880 m.	980 m.
Sp. gr. at 4°.....	1·03014	1·03104	1·03076
Solid residue (grams per litre).....	43·40	44·78	43·41
Total halogens, calculated as sodium chloride (grams per litre) .....	34·92	35·99	35·68
Insoluble "organic" iodine (mgrms. per litre) .....	0·286	0·100	0·065
Soluble "organic" iodine (mgrms. per litre) .....	1·960	2·130	1·890
Iodine in inorganic combination (mgrms. per litre)	none	0·150	0·305
Total iodine.....	2·246	2·380	2·260

From these results, it appears that the total iodine, and also the iodine existing in the form of soluble organic compounds, are practically constant at all depths. On the other hand, the iodine existing in the form of metallic iodides and iodates decreases as the surface is approached, and ultimately disappears altogether. The variation of the iodine present in an insoluble form and forming part of the substance of organised bodies is, of course, in the converse direction, the smallest amount being detected at the greatest depth, at which but few living organisms are found. The lower values found for the sp. gr. and solid residue at a depth of 980 metres compared with those at 880 metres are attributed to the influx of fresh water from springs in the bed of the ocean.

N. L.

[Presence of Iodine in Algæ and Beggiatoa.] By ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 189—194).—Examination of fresh water algæ belonging to the orders *Cyanophyceæ*, *Chlorophyceæ*, *Floridææ*, and others shows that they contain from 0·25 to 2·40 milligrams of iodine per 100 grams of the dried material, a much lower proportion than that contained by salt water forms (compare Allary, *Abstr.*, 1881, 320). *Beggiatoa* contain as much as 36 milligrams, but in lichens

the quantity is much lower than in algæ. The bacillus of tetanus contains only a minute trace of iodine, if any, and that of diphtheria none. In the case of fungi, iodine varies in amount with the nature of the food supply, and may disappear altogether. C. H. B.

**Recovery of Iodine from Waste Products.** By F. D. CHATTAWAY and K. J. P. ORTON (*J. Soc. Chem. Ind.*, 1899, 18, 560).—The material is heated on a water-bath with a sufficiency of nitrohydrochloric acid, the water, towards the last, being allowed to boil; the iodine is converted into monochloride, and no appreciable loss takes place. The iodine may be recovered from its monochloride in various ways, such as (1) by simple dilution with water, when the iodine will gradually separate in long crystals, or (2) the diluted liquid may be divided into two equal parts, the one is bleached by sulphurous acid or a sulphite, and, the other half now being added, all the iodine at once separates. If very pure iodine is required, the monochloride may be converted into nitrogen iodide, and the latter decomposed by Stas' method (compare *Proc.*, 1899, 15, 19, 21). L. DE K.

**Action of Iodine on Sulphur.** By LÉON PRUNIER (*J. Pharm.*, 1899, [vi], 9, 421—424).—Iodine readily dissolves in sulphur at a temperature of 115—120°, and the resulting mass, when cold, is crystalline. The iodine is apparently uncombined, since it volatilises at the ordinary temperature, and is readily removed by a solution of sodium thiosulphate. On adding iodine (4 parts) to plastic sulphur (1 part) kept at a temperature of 200°, much heat is developed, and a product is obtained which is different from that just described, as, on treatment with sodium thiosulphate, the iodine is but very slowly removed.

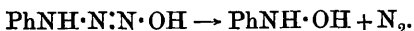
H. R. LE S.

**Action of Sodammonium and Potassammonium on Selenium.** By C. HUGOT (*Compt. rend.*, 1899, 129, 299—302. Compare *Abstr.*, 1896, ii, 21; 1898, ii, 573; this vol., ii, 151).—A mixture of selenium with sodium or potassium is treated with liquid ammonia, and when the metal is in excess a white monoselenide,  $\text{Na}_2\text{Se}$  or  $\text{K}_2\text{Se}$ , is produced, which is quite insoluble in liquid ammonia. When selenium preponderates, the monoselenide dissolves in the ammonia to form a brown solution from which a brown, crystalline polyselenide separates if the solvent is evaporated off at  $-25^\circ$  and the residue cooled to  $-55^\circ$ . These polyselenides,  $\text{Na}_2\text{Se}_4$  and  $\text{K}_2\text{Se}_4$ , are decomposed by acids, yielding hydrogen selenide and selenium.

Contrary to the statement of Franklin and Krauss (this vol., ii, 208), the author finds that selenium is insoluble in anhydrous liquid ammonia. G. T. M.

**Hydroxylamine.** By E. WAGNER (*Chem. Centr.*, 1899, i, 244—245; from *J. Russ. Chem. Soc.*, 1898, 30, 721—729).—Hydroxylamine is compared with hydrogen peroxide, and may be regarded as a derivative formed by replacing the OH by a  $\text{NH}_2$  group. Hydrogen peroxide is obtained by reducing oxygen, whilst hydroxylamine or its alkylic derivatives are formed by the reduction of oxygen derivatives of nitrogen. Both compounds are unstable, the one decomposing into water and oxygen, and the other into ammonia and oxidation products. The

alkylic derivatives of hydroxylamine act also as strong reducing agents, and in such reactions are, like hydrogen peroxide, themselves reduced. The close relationship of hydrazine to hydroxylamine is shown by the conversion of phenylazoimide into phenylhydroxylamine,  $\text{PhN} \begin{smallmatrix} \diagup \text{N} \\ \diagdown \text{N} \end{smallmatrix} \rightarrow$



On the basis of the similarity of the  $\text{NH}_2$  and  $\text{OH}$  groups, the following compounds are arranged in two series, the corresponding members of which are characterised by identical or similar behaviour, amidogen chloride,  $\text{NH}_2\text{Cl}$ , corresponding with hypochlorous acid, hydroxylamine with hydrogen peroxide, methylamine with methylic alcohol, hydrazine with hydroxylamine, nitramine with nitrous acid, &c. The oxidising and the reducing properties of the substituted hydroxylamines prepared by Bewad (*J. Russ. Chem. Soc.*, 20, 125; 21, 43) are also explained on the above theory. E. W. W.

**Inorganic Hydroxylamine Compounds.** By VOLKMAR KOHL-SCHÜTTER and KARL A. HOFMANN (*Annalen*, 1899, 307, 314—332. Compare Abstr., 1897, ii, 557; 1898, ii, 380).—*Hydroxylamine potassiouranate*,  $\text{UO}_4(\text{NH}_2\text{OH})(\text{NH}_2\text{OK}) + \text{H}_2\text{O}$ , is prepared by dissolving uranyl nitrate (10 grams) and hydroxylamine hydrochloride (15 grams) in 100 c.c. of water, and adding a 10 per cent. solution of caustic potash until the yellow, flocculent precipitate at first formed is redissolved; reddish-yellow cubes separate slowly from the liquid, precipitation being hastened by adding alcohol. The substance disintegrates to a yellow powder when heated, and has an ammoniacal smell; it is sparingly soluble in water, and is oxidised slowly by Fehling's solution. Turmeric is coloured brown by dilute solutions. When the potassium compound is digested with water which has been saturated with carbonic anhydride, the colour changes to green and hydroxylamine uranate is produced.

*Hydroxylamine sodiouranate*,  $\text{UO}_4(\text{NH}_2\text{OH})(\text{NH}_2\text{ONa}) + \text{H}_2\text{O}$ , forms minute, prismatic crystals. The mother liquor deposits the salt  $\text{UO}_4(\text{NH}_2\text{ONa})_2 + 6\text{H}_2\text{O}$ , which separates in orange-red rosettes of prisms, and dissolves in its water of crystallisation when heated; it is readily soluble in water, and vigorously reduces Fehling's solution.

The compound,  $\text{UO}_5\text{N}$ , obtained by dehydrating hydroxylamine uranate at  $125^\circ$  until the weight is constant, is a brownish-black substance with metallic lustre; cold, dilute acids liberate a mixture of nitrogen and nitrous oxide, uranic acid remaining dissolved.

The compound  $\text{MoO}_4\text{H}_2(\text{NH}_2\text{OH})_3(\text{NH}_2\text{OK})$ , is prepared by mixing aqueous solutions of ammonium molybdate (5 grams), hydroxylamine hydrochloride (10 grams), and potassium carbonate, alcohol being then added to the yellow solution; it reduces Fehling's solution and ammoniacal silver nitrate, and decomposes when heated, forming a black powder and liberating ammonia. The substance dissolves readily in water, yielding a pale yellow, neutral solution; if carbonic anhydride is passed into this liquid, hydroxylaminomolybdic acid separates in the form of a yellowish-white, flocculent precipitate. In general behaviour, the molybdenum compound differs from the hydroxylamine

uranates, and more closely resembles the vanadium derivatives already described (Abstr., 1898, ii, 381).

The compound  $\text{MoO}_5\text{N}_3\text{H}_9$ , obtained by mixing ammonium molybdate (10 grams) and hydroxylamine hydrochloride (7 grams) with 50 c.c. of 7 per cent. aqueous ammonia at  $8^\circ$ , dissolves with difficulty in water, and develops a bluish-green coloration when heated with dilute sulphuric acid.

Hydroxylamine orthophosphate,  $\text{PO}_4\text{H}_3(\text{NH}_3\text{O})_3$ , may be obtained by adding alcohol to the filtrate from a mixture of hydroxylamine sulphate and secondary barium phosphate; it is also produced from hydroxylamine hydrochloride and ammonium metaphosphate.

Hydroxylamine arsenate,  $\text{AsO}_4\text{H}_3(\text{NH}_3\text{O})_3$ , forms microscopic, rhombic prisms, yields an acid solution in hot water, and readily reduces Fehling's solution and ammoniacal silver nitrate.

M. O. F.

**Action of Hydrogen Phosphide on Copper, Cuprous Oxide, and Ammoniacal Solutions of Copper Salts.** By E. RUBÉNOVITCH (*Compt. rend.*, 1899, 128, 1398—1401. Compare this vol., ii, 102).—Hydrogen phosphide reacts with precipitated copper when the temperature is raised to  $180$ — $200^\circ$ :  $2\text{PH}_3 + 6\text{Cu} = 2\text{PCu}_3 + 3\text{H}_2$ ; the reaction with cuprous oxide occurs at the ordinary temperature, and may be thus represented:  $2\text{PH}_3 + 3\text{Cu}_2\text{O} = 2\text{PCu}_3 + 3\text{H}_2\text{O}$ . Copper phosphide is a grey, amorphous substance melting at red heat; it is soluble in nitric acid and bromine water, has no action on potassium permanganate, but is attacked by hot concentrated sulphuric acid, hydrogen phosphide and sulphurous anhydride being evolved. When exposed to oxygen at the ordinary temperature, it is slowly oxidised; at  $100^\circ$ , the reaction is attended by vivid incandescence, phosphoric anhydride and metallic copper being produced.

In aqueous solutions, hydrogen phosphide (1 mol.) reacts with copper sulphate (2 mols.) to form the phosphide  $\text{P}_2\text{Cu}_5 + \text{H}_2\text{O}$ , and with copper acetate or formate ( $2\frac{1}{2}$  mols.) to form the compound  $\text{PCu}_3\text{O}$ ; it has no action on aqueous cupric chloride. In ammoniacal solutions from which air is excluded, the reaction with hydrogen phosphide is common to all copper salts, and in the case of the chloride may be represented thus:  $6\text{PH}_3 + 12\text{CuCl}_2 + 6\text{H}_2\text{O} + 24\text{NH}_3 = 4\text{PCu}_3 + \text{H}_3\text{PO}_4 + \text{H}_3\text{PO}_2 + 24\text{NH}_4\text{Cl}$ . In every case, 2 mols. of the salt react with 1 of the phosphide, and the copper phosphide produced is identical with that obtained from metallic copper or cuprous oxide. If oxygen be admitted after the precipitation of the copper phosphide, the latter will dissolve, and the amount of oxygen required for complete solution is equal to twice the volume of the hydrogen phosphide originally absorbed.

G. T. M.

**Reducing Properties of Boron and Silicon.** By ANDRÉ DUBOIN and ARMAND GAUTIER (*Compt. rend.*, 1899, 129, 217—218).—When chlorine is passed over a red hot mixture of aluminium oxide and boron, obtained by the action of aluminium on boric anhydride, aluminium chloride and boric anhydride are the products; similar results are obtained with bromine and with iodine vapour mixed with

hydrogen, whilst hydrogen sulphide yields boron sulphide. A mixture of aluminium oxide and silicon, obtained in a similar way, yields aluminium chloride, and not silicon chloride or silicochloroform, when heated to bright redness in a current of hydrogen chloride. When intimately mixed with aluminium oxide, boron or silicon therefore behave in the same way as carbon under the conditions described. C. H. B.

**Preparation of Graphitoidal Silicon.** By FREDERICK S. HYDE (*J. Amer. Chem. Soc.*, 1899, 21, 663—665).—Finely powdered white sand is heated in a test-tube with magnesium powder, the brownish-black product is then powdered and fused in a Denver crucible with aluminium and cryolite. The product, consisting of an alloy of aluminium and silicon, is treated with warm hydrochloric acid, and the silicon obtained in black, glistening spangles. J. J. S.

**Carbonic Anhydride on Mont Blanc.** By MAURICE DE THIERRY (*Compt. rend.*, 1899, 129, 315—316. Compare *Abstr.*, 1897, ii, 253).—The results indicate that the amount of carbonic anhydride in the atmosphere varies only very slightly with changes of altitude; at altitudes of 1080 and 3050 metres, the amounts were respectively 26.2 and 26.9 litres per 100 cubic metres of air. G. T. M.

**Argon and its Combinations.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 71—84).—A record of experiments on the effect of the silent electric discharge on a mixture of argon with various organic compounds. The mixture was enclosed in an annular space formed by two concentric tubes, the distance between their surfaces being from 0.5 to 0.2 mm. The discharge was obtained from a Ruhmkorff coil, which was connected to a Leyden jar and fed by three or six accumulators (6.3 to 12.6 volts), the coil being so adjusted that its maximum spark was from 6 to 8 mm. long. The volume of argon varied from 5 to 10 c.c., and that of the organic compound, when a liquid, from 0.1 to 0.2 c.c.

Ethylene, glycollic ether, acetaldehyde, acetone, amylene, light petroleum, propionitrile, allylic thiocyanate, and amylamine were the members of the fatty series employed, and in no case was luminosity produced or any absorption of argon observed. Various decomposition products were formed; for example, methane, carbonic anhydride, and hydrogen were obtained in the experiment with glycollic ether, and in that with amylamine an odour of piperidine was noticed.

Benzene, toluene, cymene, terebenthene, anisole, phenol, benzaldehyde, aniline, phenylic thiocyanate, and benzonitrile, as representative of the benzene series, gave results quite different from those obtained with members of the fatty series; a more or less intense green luminosity or glow was seen, accompanied by a decided absorption of argon. On spectroscopic examination, the characteristic lines of argon, mercury, carbon, and hydrogen were observed. The absorption of argon varied from 8 (for benzene) to 1 (for aniline) per cent. of the volume employed, and is attributed to the formation of a compound of argon, termed *phenylmercurargon*, possessing a low vapour tension, and depending for its production on the vapour tension of the organic compound which gives rise to it, and on certain complex conditions of stability and dissociation.

Absorption of argon was uncertain with furfuraldehyde and pyrroline,

but amounted to 2—3 per cent. with thiophen and pyridine. The feeble, green luminosity produced in all four cases was most marked with furfuraldehyde and pyridine.

The action of argon on benzene and carbon bisulphide has also been studied more minutely (compare Abstr., 1895, i, 412; ii, 469, 498). With benzene, the luminosity and absorption appear at the same time, and the maximum absorption is about 8 per cent. of the volume of argon employed. When the temperature of the space through which the discharge takes place is too high, the phenylmercurargon compound is not obtained; also, if the volume of liquid benzene is equal to that of the argon, luminosity is not produced, even after 24 hours, possibly in consequence of the absorption of the phenylmercurargon compound by the hydrocarbon. The green luminosity immediately disappears when the electric discharge is stopped, although, if the experiment is made at twilight, a violet glow is seen for a fraction of a second, and then dies out, giving place to the permanent yellow tint of the polymerised derivative of benzene along the sides of the tube.

In the case of carbon bisulphide, it was found that, with an E.M.F. of 6.3 volts, 7 per cent. of argon was absorbed, and a fawn-coloured, solid compound was produced; with an E.M.F. of 12.6 volts, however, there was no absorption, even after 24 hours, and the product was black and carbonaceous. When a mixture of argon, hydrogen, and carbon bisulphide was subjected to the action of the silent discharge, the hydrogen disappeared in the course of 24 hours, and argon was absorbed to the extent of 10 per cent.; with a mixture of argon and equal volumes of carbon bisulphide and benzene, the amount of argon absorbed was 9 per cent.

The amounts of hydrogen, nitrogen, and argon absorbed by carbon bisulphide under the influence of the silent electric discharge were determined (see this vol., ii, 648).  
H. R. LE S.

**Influence of Various Substances in Solution on the Crystalline Form of Sodium Chloride.** By P. ORLOFF (*Zeit. Kryst. Min.*, 1899, 31, 516; from *J. Russ. Chem. Soc.*, 1896, 28, 715—774).—To determine the influence of the character of the solution on the form of crystals, numerous substances were mixed with aqueous solutions of sodium chloride, and the different forms—cube, octahedron, icositetrahedron—of the sodium chloride crystals obtained were noted. The presence of hydrochloric acid gives rise to elongated (acicular) cubes. The author considers that the influence on the form of the crystals is due to the alteration of the character of the solution by the formation of various hydrates and double salts.

Attempts to prepare  $\text{NaCl} + 10\text{H}_2\text{O}$  were unsuccessful. L. J. S.

**Basic Silver Copper Salts.** By PAUL SABATIER (*Compt. rend.*, 1899, 129, 211—213).—The action of silver oxide on a solution of cupric nitrate yields the same compound,  $3\text{Cu}(\text{OH})_2 \cdot 2\text{AgNO}_3$ , as is formed by the action of cupric hydroxide on silver nitrate (Abstr., 1897, ii, 553). The rate of action of silver nitrate solution on cupric hydroxide varies with its concentration. A very concentrated solution acts rapidly on either the blue or the brown hydroxide, and forms pale blue, slender needles of a compound,  $2\text{Cu}(\text{OH})_2 \cdot 2\text{AgNO}_3$ .

Cupric hydroxide and silver chlorate, or silver oxide and cupric



chlorate, yield the compound  $2\text{Cu}(\text{OH})_2, 2\text{AgClO}_3$  in prismatic leaflets. With silver oxide and an excess of cupric chlorate, the compound  $3\text{Cu}(\text{OH})_2, \text{Cu}(\text{ClO}_3)_2$  is formed.

Cupric hydroxide and silver sulphate yield the compound  $3\text{Cu}(\text{OH})_2, \text{Ag}_2\text{SO}_4$  in short prisms, or the hydrated salt,  $3\text{Cu}(\text{OH})_2, \text{Ag}_2\text{SO}_4 + 3\text{H}_2\text{O}$ , in long needles.

The double basic dithionate,  $2\text{Cu}(\text{OH})_2, \text{Ag}_2\text{S}_2\text{O}_6$ , is a very bulky, flocculent, violet-blue product. C. H. B.

**Agents for Removing Lime and Magnesia from Natural Waters for Industrial Purposes.** By MARTIN L. GRIFFIN (*J. Amer. Chem. Soc.*, 1899, 21, 665—678. Compare this vol., ii, 476).—Comparative experiments have been made with sodium hydroxide, sodium aluminate, barium hydroxide, sodium phosphate, and sodium fluoride as reagents for removing lime and magnesia from natural waters. The results indicate that waters containing from 0.020 to 0.025 gram calcium oxide, and from 0.005 to 0.007 gram magnesium oxide cannot be appreciably purified, although frequently the amounts of these impurities can be reduced below these limits in the case of waters highly charged. The most effectual reagents for removing calcium carbonate are sodium hydroxide and sodium fluoride, and in certain cases sodium aluminate. Waters containing a large proportion of calcium sulphate and carbonate can also be successfully treated with the same reagents; barium hydroxide does not give such satisfactory results. The most useful reagent for removing magnesium salts is sodium hydroxide, then follows barium hydroxide. Sodium fluoride is of no use for removing magnesium salts, but is to be recommended when large quantities of calcium sulphate and chloride are present. Barium hydroxide is most serviceable in the treatment of acid mine waters.

J. J. S.

**Arsenides of Strontium, Barium, and Lithium.** By PAUL LEBEAU (*Compt. rend.*, 1899, 129, 47—50).—The method of preparing calcium arsenide by reducing calcium arsenate with petroleum coke at the temperature of the electric furnace (this vol., ii, 288) has now been successfully applied to the production of the arsenides of strontium, barium, and lithium. *Strontium arsenide*,  $\text{Sr}_3\text{As}_2$ , is thus obtained as a crystalline mass which is transparent and reddish-brown in thin sections, has a sp. gr. 3.6 at  $15^\circ$ , and closely resembles the corresponding calcium compound in its reactions. It is attacked by fluorine at the ordinary temperature with incandescence and production of arsenious fluoride, and a similar reaction takes place with chlorine at  $160^\circ$ , with bromine at  $200^\circ$ , and with iodine vapour at higher temperatures. Vivid combustion also occurs when the arsenide is heated to dull redness in oxygen and in sulphur vapour. It is converted into strontium carbide when heated with carbon in the electric furnace. In contact with water, it is decomposed, with production of strontium hydroxide and hydrogen arsenide. Strontium arsenide reduces most metallic oxides and is violently attacked by oxidising agents. Barium arsenide,  $\text{Ba}_3\text{As}_2$ , has a sp. gr. 4.1 at  $15^\circ$ , and is somewhat darker in colour and more fusible than the arsenides of calcium and strontium; it also displays greater chemical activity. It

burns at the ordinary temperature in fluorine, chlorine, or bromine, in oxygen at  $300^{\circ}$ , and in sulphur vapour below a dull red heat. *Lithium arsenide*,  $\text{Li}_3\text{As}$ , forms a dark brown, crystalline mass, which is transparent and reddish-brown in thin sections. It is attacked by fluorine, chlorine, bromine, or iodine at the ordinary temperature with incandescence, burns vividly when heated in oxygen at a temperature below redness, reacts violently with nitric acid, and reduces most metallic oxides at a low temperature. Attempts to prepare the arsenides of potassium and sodium were unsuccessful, these compounds being apparently unstable under the experimental conditions employed.

N. L.

**Action of Magnesium on Solutions of its Salts.** By GEORGES LEMOINE (*Compt. rend.*, 1899, 129, 291—294).—Hydrogen is evolved when magnesium is added to a solution of one of its salts. The evolution ceases when the metal becomes coated with a deposit of hydrated magnesium oxide, but recommences if, after filtering, more of the metal is added to the solution, the maximum quantity of hydrogen obtainable being about 42 per cent. of the total amount present in the water. In very dilute solutions, the action may continue for several months, but with greater concentrations it ceases after 2 or 3 days. The alteration in composition is very slight when solutions of the acetate or chloride are employed; with the sulphate, a partial precipitation occurs owing to the formation of basic salt. When excess of magnesium is added to an acid, hydrogen is rapidly evolved during the formation of the salt; this action is followed by a slower evolution of gas arising from the interaction of the salt and the metal. The phenomenon is probably due to hydrolytic dissociation of the salt into magnesium oxide and free acid; the latter acts on the metal, an oxy-salt being formed as an intermediate product; this decomposes into normal salt and oxide, the latter is precipitated, and the cycle of changes is repeated.

A similar behaviour with solutions of its salts is exhibited by aluminium, but not by zinc or cobalt.

G. T. M.

**Hydrates of Magnesium Chloride.** By ALEXIS BOGORODSKY (*Chem. Centr.*, 1899, i, 245—246; from *J. Russ. Chem. Soc.*, 1898, 30, 735—740).—Van't Hoff and Meyerhoffer have shown from theoretical considerations that magnesium chloride should form the hydrates,  $\text{MgCl}_2 + 8\text{H}_2\text{O}$  and  $\text{MgCl}_2 + 12\text{H}_2\text{O}$ , and hydrates of these compositions have now been prepared. When a solution of magnesium chloride in water (10 mols.) is cooled to  $20^{\circ}$ , both hydrates separate out, but on removing the mass from the vessel the dodecahydrate disappears and the octohydrate remains as a coarse, crystalline powder, which, when mixed with the original solution cooled to  $-10^{\circ}$  or  $-12^{\circ}$ , forms thick, crystalline plates. As this hydrate decomposes at  $-9.8^{\circ}$ , it is probably an isomeride of Van't Hoff and Meyerhoffer's compound which decomposes at  $-3.4^{\circ}$ . The *dodecahydrate* is obtained in large crystals by adding a crystal of the hydrate to a solution of magnesium chloride in about 12.06 mols. of water. The crystals are lighter than the mother liquor, and, according to the author, this is the first time that increase in volume has been observed in the formation of a hydrate.

The hydrate may also separate from solutions which contain smaller proportions of water than the hydrate itself. It melts without decomposing at  $-16^{\circ}$ , and on becoming liquid absorbs a large amount of heat. It may be assumed therefore that hydrates which melt without visible decomposition may exist also as liquids between certain limits of temperature. E. W. W.

**Electrolysis of Fused Zinc Chloride.** By HERMANN S. SCHULTZE (*Zeit. anorg. Chem.*, 1899, 20, 323—332).—When fused zinc chloride is electrolysed with carbon electrodes, chlorine is evolved at the anode and hydrogen at the cathode, whilst the electrolyte is rendered cloudy by the separation of a bluish-grey substance. After a time, the evolution of hydrogen stops, zinc is deposited instead, and the separation of the bluish-grey substance ceases. The author has observed the same phenomena when a piece of the purest zinc is introduced into fused zinc chloride: thus the cloudiness of the latter cannot be due to the carbon electrodes.

Zinc chloride obstinately retains traces of water, and this probably reacts with zinc according to the equation  $\text{Zn} + \text{H}_2\text{O} = \text{ZnO} + \text{H}_2$ ; analysis confirms this, and shows that when the action continues the zinc oxide contains an excess of zinc beyond that required for  $\text{ZnO}$ , whence the darkening in colour. A specimen of zinc chloride which evolved hydrogen but from which zinc oxide did not separate was found to contain hydrochloric acid. According to the method of preparation, zinc chloride may contain water or hydrochloric acid, and of these only the former interferes with a smooth electrolysis of the fused salt.

J. C. P.

**Orthoplumbates of the Alkaline Earths. III. A New, Higher Oxide of Lead.** By GEORG KASSNER (*Arch. Pharm.*, 1899, 237, 409—426).—Grützner and Höhnel's calcium metaplumbate (*Abstr.*, 1896, ii, 248) has the composition which they assigned to it; at  $300^{\circ}$ , it loses only  $3/4$  of its water.

When calcium metaplumbate is heated for a considerable time at  $250^{\circ}$  in a current of pure dry air, its loss of weight is less than the weight of the water given off. This is due to absorption of oxygen; the residue, a reddish-brown powder, evolves oxygen when treated with water, but more rapidly when treated with dilute nitric acid; in the latter case, lead dioxide is left undissolved, and lead and calcium nitrates go into the solution; at  $330^{\circ}$ , the compound is also decomposed. Probably this residue contains a small amount of a compound,

$\text{Ca} \begin{smallmatrix} \text{O} \cdot \text{PbO} \cdot \text{O} \\ \text{O} \cdot \text{PbO} \cdot \text{O} \end{smallmatrix}$  or calcium perplumbate, as it may be called. For the

corresponding oxide,  $\text{O} \begin{smallmatrix} \text{PbO} \cdot \text{O} \\ \text{PbO} \cdot \text{O} \end{smallmatrix}$ , it is proposed to reserve the name lead peroxide or superoxide, which ought not to be given to the dioxide,  $\text{PbO}_2$ , as this has not the character of a true peroxide such as hydrogen peroxide. C. F. B.

**Dissociation of Diammonio-mercuric Iodide.** By MAURICE FRANÇOIS (*Compt. rend.*, 1899, 129, 296—299).—Two phases may be distinguished in the dissociation of diammoniomercuric iodide,  $\text{HgI}_2 \cdot 2\text{NH}_3$ ; the first corresponds with the formation of an inter-

mediate compound,  $3\text{HgI}_2 \cdot 4\text{NH}_3$ , and the second with the decomposition of this into mercuric iodide and ammonia. The first phase is characterised by high and the second by low dissociation pressures; in both, the pressure is constant for a given temperature, and increases as the latter is raised. At  $25^\circ$ , the compounds  $\text{HgI}_2 \cdot 2\text{NH}_3$  and  $3\text{HgI}_2 \cdot 4\text{NH}_3$ , like the ammonio-silver chlorides (Jarry, Abstr., 1897, ii, 259), have the same dissociation pressure in aqueous solution as in a vacuum.

G. T. M.

**Hydrates of Manganous Chloride.** By P. KUZNETZOFF (*Chem. Centr.*, 1899, i, 246; from *J. Russ. Chem. Soc.*, 1898, 30, 741—748).—When the tetrahydrate of manganous chloride,  $\text{MnCl}_2 + 4\text{H}_2\text{O}$ , is slowly heated, it decomposes at  $58^\circ$ , forming a pink powder and a liquid, and at  $120^\circ$  it is not completely melted (compare Brandes, *Ann. Chim. Phys.*, 1881, [v], 22, 563). The product formed at  $58^\circ$  may be cooled to  $23^\circ$  without change, but below this temperature the tetrahydrate is regenerated. The dihydrate,  $\text{MnCl}_2 + 2\text{H}_2\text{O}$ , prepared by heating the tetrahydrate in filter paper at  $60$ — $63^\circ$  for  $1\frac{1}{2}$ —1 hour, is a pale pink substance, loses water at  $70^\circ$ , and when exposed to the air for two months is converted into the tetrahydrate.

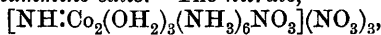
When the crystals, obtained by cooling a solution of the composition  $\text{MnCl}_2 + 11\cdot7\text{H}_2\text{O}$  to  $-37^\circ$  are added to another portion of the same solution at  $-21^\circ$ , the hexahydrate,  $\text{MnCl}_2 + 6\text{H}_2\text{O}$ , separates after 48 hours as a light pink, crystalline powder containing crystals up to 5 cm. long. From a solution,  $\text{MnCl}_2 + 10\cdot35\text{H}_2\text{O}$ , the tetrahydrate, mixed with traces of the hexahydrate, separates, and a solution,  $\text{MnCl}_2 + 9\cdot17\text{H}_2\text{O}$ , yields only the tetrahydrate. On the other hand, a solution,  $\text{MnCl}_2 + 12\text{H}_2\text{O}$ , even when cooled to  $-48^\circ$ , only yields the hexahydrate with difficulty. At  $-2^\circ$ , the hexahydrate decomposes with the tetrahydrate.

From a comparison of the hydrates of manganous, ferrous, cobaltous, and nickelous chlorides, it is seen that the greater the atomic weight of the metal the greater is the stability of the hydrate.

E. W. W.

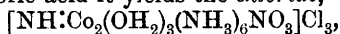
**Constitution of Inorganic Compounds. XVI. Complex Cobaltammonium Compounds.** By ALFRED WERNER, F. STEINITZER, and K. RÜCKER (*Zeit. anorg. Chem.*, 1899, 21, 96—115).—*Sulphatoimido-octamminedicobalt chloride*,  $[\text{NH}:\text{Co}_2(\text{OH}_2)(\text{NH}_3)_8\text{SO}_4]\text{Cl}_2 + 2\text{H}_2\text{O}$ .—When the nitrate of the hydrosulphatoimido-octamine series is rubbed with hydrochloric acid, the salt,  $[\text{NH}:\text{Co}_2(\text{NH}_3)_8\text{SO}_4]\text{Cl}_3 + 2\text{H}_2\text{O}$ , is obtained in lustrous, violet crystals which can be recrystallised from water. This salt, when heated for 6 hours at  $110^\circ$ , loses 1 mol. of hydrogen chloride, and is converted into the sulphatochloride, a small quantity of imido-octamminedicobalt sulphate being formed at the same time. A similar reaction takes place when the hydrosulphatonitrate is treated with concentrated ammonia and *sulphatoimido-octamminedicobalt nitrate*,  $[\text{NH}:\text{Co}_2(\text{OH}_2)(\text{NH}_3)_8\text{SO}_4](\text{NO}_3)_2 + 2\text{H}_2\text{O}$ , is obtained.

*Nitratoimidohexamine salts.*—The nitrate,



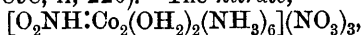
is obtained by adding fuming nitric acid to a warm aqueous solution

of tetraquoimido-hexamminedicobalt nitrate. When treated with hot hydrochloric acid, it is converted into the imido-hexammine chloride; with cold hydrochloric acid it yields the *chloride*,

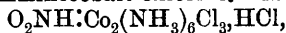


which crystallises in lustrous, reddish-yellow leaflets.

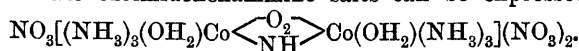
The authors have obtained two new series of compounds which contain the peroxide group, and they name them ozocobalt- and diozocobalt-salts. The *ozoimido-hexamminedicobalt* salts are obtained in the conversion of crude melano-chloride into nitrate after the separation of the imidotetraquo-hexammine salt, when the nitrate of the new series separates from the mother liquors in dark green crystals (Abstr., 1898, ii, 226). The *nitrate*,



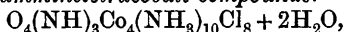
crystallises in dark green leaflets, and in aqueous solution yields, with hydrochloric acid, a sparingly soluble chloride, with hydrobromic acid the corresponding bromide, and with potassium cyanide a brown precipitate. Sulphurous acid converts it into a red compound which, when evaporated with hydrochloric acid, yields cobaltous salts and a small quantity of a sparingly soluble, green salt which is probably a dichlorotetrammine salt, whilst when treated with fuming nitric acid it yields a red salt which, when crystallised from hydrochloric acid, yields dichloro-aquotriamminedicobalt chloride. The *chloride*,



a heavy, black, crystalline powder, can be recrystallised from dilute hydrochloric acid and is acid, being in this respect similar to the imido-hexammine chloride. The reactions of the nitrate of the new series with fuming nitric acid show that the six ammonia groups are symmetrically disposed with regard to the two cobalt atoms, thus,  $(\text{NH}_3)_3\text{Co}-\text{NH}-\text{Co}(\text{NH}_3)_3$ , and since the ozoimido-hexammine salts bear the same ratio to the imido-hexamminedicobalt salts as the anhydro-oxycobalt salts bear to the aquopentammine salts, the constitution of the ozoimido-hexammine salts can be expressed by the formula



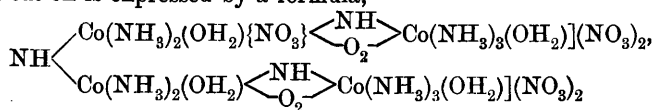
*Diozotri-imidodecamminetetracobalt compounds.*—The *chloride*,



is obtained by dissolving oxycobaltammine nitrate (300 grams) in water (2 litres) at 50°, and, after filtration, diluting with an equal bulk of water, adding 4 litres of concentrated hydrochloric acid, and then passing a current of air through the solution for some hours. The black, crystalline precipitate of the crude chloride mixed with imido-hexammine chloride, after washing with alcohol and ether, is converted into the nitrate and reconverted into the chloride. It is a black, crystalline powder sparingly soluble in cold water, more easily in warm water, is partially decomposed when heated with water at 60–70°, completely so when boiled, and gives brown, flocculent precipitates with platinic chloride and mercuric chloride. It is not decomposed by dilute acids or by concentrated hydrochloric acid. The *bromide* is a black, crystalline powder, similar to the chloride. The *nitrate*, obtained by treating the chloride dissolved in dilute nitric acid with silver nitrate, crystallises in beautiful, black, tetrahedral

forms, and has the composition  $O_4(NH)_3Co_4(NH_3)_{10}(OH_2)_4(NO_3)_5 + H_2O$ . When treated with warm concentrated nitric acid, it yields cobaltous salts and a bright red salt which, when treated with hydrochloric acid, is converted into the dichloroaquotriammine chloride. When treated with nitrous acid, it yields an imido-hexammine salt, probably nitrato-triaquaimido-hexammine nitrate, and the mother liquors of this salt, when treated with hydrochloric acid, yield the dichlorotetrammine chloride and a dark coloured salt of unknown composition.

The diozocobalt salts have probably a constitution similar to the ozocobalt salts; a comparison of their composition shows that they are formed by the combination of 2 mols. of the ozo-salt with elimination of 1 mol. of ammonia and the addition of 1 mol. of water. In the diozo-series, 3 imido-groups are present, and, considering the decomposition products obtained from the diozo-salts by the action of sulphurous, nitric, and nitrous acids, it is most probable that their constitution is expressed by a formula,



indicating the union of 2 molecules of ozo-salt by an imido-group.

E. C. R.

**Constitution of Inorganic Compounds. XVII. Oxalato-diethylenediamminecobalt Salts.** By ALFRED WERNER and A. VILMOS (*Zeit. anorg. Chem.*, 1899, 21, 145—158).—*Oxalato-diethylenediamminecobalt chloride*,  $[Co(C_2O_4)C_2H_4(NH_2)_2]Cl + 3H_2O$ , obtained by heating dichlorodiethylenediamminecobalt chloride (praseo-salt), dissolved in a small quantity of water, with oxalic acid until the green solution changes to red, is precipitated from the cold solution by alcohol. It crystallises in thin, red leaflets or ruby-red, four-sided prisms, effloresces on exposure to the air, is fairly soluble in cold, easily so in hot water, and insoluble in alcohol. It is not decomposed when heated at  $130^\circ$ , or when treated with concentrated sulphuric acid, and gives no precipitate with calcium chloride. With sodium dithionate, it yields a precipitate of bright red leaflets; with potassium dichromate, orange-red, six-sided leaflets; with ammonium oxalate and potassium iodide, precipitates which distinguish it at once from the corresponding tetrammine salt. The *mercurichloride*,  $Co(C_2O_4)(C_2H_8N_2)HgCl_3$ , crystallises in red, lustrous leaflets insoluble in water; the *aurichloride* is a bright orange yellow, insoluble powder. The *base*,  $[Co(C_2O_4)C_2H_8N_2]OH$ , obtained in aqueous solution by the action of freshly-prepared silver oxide on a solution of the chloride, gives a cherry red solution, is strongly alkaline, absorbs carbonic anhydride from the air, precipitates metallic hydroxides from solutions of salts of zinc, copper, &c., and is very stable. The *bromide* crystallises in dark red leaflets; the *iodide*, which is obtained mixed with a dark violet, insoluble periodide, crystallises in red, lustrous leaflets and is sparingly soluble in water. The *thiocyanate* separates from hot water in dark red, lustrous crystals; the *nitrate* crystallises from solutions above  $30^\circ$  without water of crystallisation in dark red

aggregates, but below  $30^{\circ}$ , with  $2\text{H}_2\text{O}$ , in aggregates of pale red needles, and is soluble in 400 parts of water at  $0^{\circ}$ ; the *hydrogen sulphate* crystallises, with  $1\text{H}_2\text{O}$ , in aggregates of slender, red needles and has an acid reaction; the *sulphate*, with  $4\text{H}_2\text{O}$ , separates in large, brownish-red crystals, is very soluble in water, and effloresces on exposure to the air; the *oxalate*, with  $2\text{H}_2\text{O}$ , crystallises in rose-coloured needles, is neutral, and easily soluble in water.

E. C. R.

**Hydroxylamine Compound of Nickel Sulphate.** By RUDOLF UHLENHUTH (*Annalen*, 1899, 307, 332—334).—When purified hydroxylamine is added to a cold, saturated solution of nickel sulphate, the green colour gradually changes to azure blue, becoming finally transformed into deep red, resembling the colour of ferric thiocyanate; if a few drops of alcohol are then added, the compound,  $\text{NiSO}_4 + 6\text{NH}_2\cdot\text{OH}$ , separates in red, quadratic crystals. The substance is decomposed by water, and reduces Fehling's solution.

M. O. F.

**Action of Nitric Oxide on Chromous Salts.** By GABRIEL CHESNEAU (*Compt. rend.*, 1899, 129, 100—103).—When nitric oxide is passed into blue chromous chloride solution, protected from the air by a layer of petroleum (sp. gr. 0.87) 0.1—0.5 mm. in depth, heat is developed and the liquid becomes dark red, changing to a greenish-brown in from 1 to 2 hours at the ordinary temperature, and immediately if heated to  $100^{\circ}$ . No gas is evolved when the resulting solution is heated or placed in a vacuum. When a rapid current of the gas is passed into the solution, the amount absorbed is from 1.2 to 1.3 mols. NO for every 3 mols.  $\text{CrCl}_2$ , a proportion corresponding with that required for the formula  $3\text{CrCl}_2\cdot\text{NO}$ ; with a slow current of the gas, the absorption is less, being only 0.87 mol. NO for every 3 mols.  $\text{CrCl}_2$ . This difference is attributed to a secondary action between unchanged chromous salt and the newly formed compound, because the solution through which a rapid current of the gas has been passed, after exposure to the air to ensure the oxidation of any uncombined chromous chloride, precipitates cuprous oxide from Fehling's solution, but gives no ammonia by Schlöesing's method, whereas that prepared by passing a slow current of the gas gives no precipitate with Fehling's solution, but evolves ammonia on heating with an alkali. The reactions involved under the two conditions are represented respectively by the equations  $2[(\text{CrCl}_2)_3\text{NO}] + 3\text{H}_2\text{O} = 3\text{Cr}_2\text{Cl}_4\text{O} + 2\text{NH}_3\text{O}$ ;  $2[(\text{CrCl}_2)_3\text{NO}] + 2\text{CrCl}_2 + 3\text{H}_2\text{O} = 4\text{Cr}_2\text{Cl}_4\text{O} + 2\text{NH}_3$ .

H. R. LE S.

**Chromic Acetate.** By ALBERT RECOURA (*Compt. rend.*, 1899, 129, 158—161. Compare *Abstr.*, 1897, ii, 172; this vol., ii, 226, 339).—Chromic acetate exists in four isomeric modifications. A solution of the normal salt is best prepared by the double decomposition of equivalent quantities of violet chromic sulphate and barium acetate. From the green solution so obtained, the author has isolated the salt  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 + 5\text{H}_2\text{O}$ . That this substance is a normal, and not a basic, salt is proved by the fact that it requires exactly 3 mols. of sodium hydroxide for the complete decomposition of 1 mol. of the

acetate, chromic hydroxide being precipitated. Moreover, when a solution containing 1 mol. of the acetate is treated with an equivalent amount of dilute sulphuric acid, the heat evolved (12·17 Cals.) corresponds exactly with that required for the displacement of the whole of the acetic acid by sulphuric acid. The normal salt may also be obtained by dissolving freshly precipitated chromic hydroxide in the calculated amount of acetic acid.

The green solution of the normal salt gradually changes colour, and at the end of a few hours is pure violet in shade; this corresponds with the first phase of transformation. The violet colour then changes in tint during about a fortnight, the change corresponding with the second phase of transformation. The third phase requires about a year for its completion, and during this time the violet colour gradually changes to green. These colour changes correspond with the gradual conversion of the normal salt into three isomerides. In the liquid resulting from the first phase of transformation, only two of the acid radicles react with sodium hydroxide, that is, only two exist as electropositive ions, the third remaining combined with the chromium, whilst in the liquids resulting from the second and third phases only one exists in the ionic state.

H. R. LÉ S.

**Isomeric Modifications of Chromic Acetate.** By ALBERT RECOURA (*Compt. rend.*, 1899, 129, 208—211. Compare preceding abstract).—Normal chromic acetate is best prepared by mixing freshly precipitated chromic hydroxide with the equivalent quantity of glacial acetic acid, the product being collected immediately by means of a pump, and dried on porous plates. It is a grey-lilac powder, which forms a yellowish-green solution identical with that obtained by the interaction of violet chromic sulphate and barium acetate, but changes very rapidly to one of the abnormal violet acetate.

The violet monacid acetate (*loc. cit.*) is obtained by allowing a solution of the violet acetate to evaporate over sulphuric acid in presence of acetic acid. It forms thin, brilliant, vitreous, violet lamellæ, of the composition  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 + \text{H}_2\text{O}$ , and when exposed to air slowly loses 1 mol. of acetic acid. When treated with sodium hydroxide, chromium is not precipitated, and the compound behaves like a monobasic acid. Thermochemical measurements show that the chromic radicle is not decomposed by sulphuric acid. The heat of neutralisation by sodium hydroxide is 13·25 Cals., which approximates to that of acetic acid, 13·40 Cals., and the difference is not due to errors of experiment, but shows that the third molecule of acetic acid is not dissociated from the rest of the compound in solution. This is confirmed by cryoscopic observations, the difference between the molecular reduction of the acetate and the product formed by neutralising it with sodium hydroxide being identical with the difference between the molecular reduction of acetic acid and sodium acetate respectively; the actual values of the molecular reductions also approximate somewhat closely. It follows that this abnormal chromic acetate is to be regarded as a complex monobasic acid,  $\text{Cr}(\text{C}_2\text{H}_3\text{O})_2, \text{C}_2\text{H}_4\text{O}_2 + 2\text{H}_2\text{O}$ , containing the radicle  $\text{Cr}(\text{C}_2\text{H}_3\text{O})_2$ , and the author calls it *chromomonacetic acid*.

C. H. B.



**Isomeric Modifications of Chromic Acetate.** By ALBERT RECOURA (*Compt. rend.*, 1899, 129, 288—291. Compare preceding abstracts).—When an aqueous solution of ordinary chromic acetate is left for several hours, its colour changes from green to violet, an isomeride being produced. This substance, *chromodiacetic acid*,  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2\text{C}_2\text{H}_4\text{O}_2$ , has not been isolated in the solid state, but its existence is inferred from the alterations in the properties of the solution. Alkalis no longer produce a precipitate, and 2 mols. of caustic soda are required to neutralise a solution originally containing 1 mol. of chromic acetate, the heats of neutralisation being 12·8 and 9·7 Cals. for the first and second molecules respectively. Cryoscopic observations also indicate that the solution contains the complex molecule, and not chromium acetate and free acetic acid.

The green isomeride, which is formed when a solution of chromic acetate is left for 12 months (*loc. cit.*), can be more rapidly obtained by heating to the boiling point a solution of chromic acetate (1 mol.) with acetic acid (3 mols.). The green solution, on evaporation over sulphuric and acetic acids, yields a green solid which has the composition  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 + \frac{1}{2}\text{H}_2\text{O}$ . This *green* chromomonacetic acid differs from its violet isomeride in containing half the amount of water; the heat of neutralisation by soda is 12·54 Cals. instead of 13·25, and different varieties of chromium hydroxide are precipitated when they are boiled with solutions of the caustic alkalis.

The paper concludes with a summary of the properties of the four isomeric forms of chromic acetate. G. T. M.

**Metallic Thioantimonites.** By POUGET (*Compt. rend.*, 1899, 129, 103—104. Compare Abstr., 1897, ii, 499 and 500).—When a dilute solution of potassium thioantimonite is added to a solution of a salt of zinc, manganese, or lead, a voluminous precipitate of the trimetallic thioantimonite,  $\text{Zn}_3\text{Sb}_2\text{S}_6$  (orange),  $\text{Mn}_3\text{Sb}_2\text{S}_6$  (dirty rose), or  $\text{Pb}_3\text{Sb}_2\text{S}_6$  (maroon) is produced. With a concentrated solution of potassium thioantimonite, the same compounds are formed, but if the potassium salt is in excess these precipitates are rapidly converted into crystalline compounds of the composition  $\text{ZnKSbS}_3$  (white),  $\text{MnKSbS}_3$  (rose), or  $\text{PbKSbS}_3$  (maroon) respectively. These are easily decomposed by water, forming crystalline, trimetallic thioantimonites.

The compounds  $\text{Fe}_3\text{Sb}_2\text{S}_6$ ,  $\text{Ni}_3\text{Sb}_2\text{S}_6$ , and  $\text{Co}_3\text{Sb}_2\text{S}_6$ , precipitated from solutions of salts of ferrous iron, nickel, and cobalt respectively, are very easily oxidised, and always contain potassium if prepared from concentrated solutions.

A dilute solution of potassium thioantimonite added to a solution of a copper salt gives a black precipitate of  $\text{Cu}_3\text{Sb}_2\text{S}_6$ , provided the copper is in excess; if, however, the potassium thioantimonite is in excess, the precipitate first formed is eventually reduced to  $\text{Cu}_3\text{SbS}_3$ . With concentrated solutions of potassium thioantimonite, the black precipitate rapidly changes to  $\text{Cu}_2\text{KSbS}_3$ , a yellow, crystalline compound, which is easily decomposed by water, forming the reddish-brown compound  $\text{Cu}_3\text{SbS}_3$ .

Potassium thioantimonite precipitates metallic mercury from a solution of a mercuric salt. H. R. LE S.

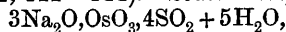
**A Ruthenium Potassium Nitrite.** By L. BRIZARD (*Compt. rend.*, 1899, 129, 216—217).—When a dilute and slightly warm solution of the complex chloride,  $\text{Ru}_2\text{H}_2(\text{NO})\text{Cl}_3 \cdot 3\text{KCl} \cdot 2\text{HCl}$ , slightly acidified with hydrochloric acid, is mixed with successive small quantities of potassium nitrite until liberation of nitrogen oxides ceases, its colour changes from red to orange-yellow, and, after concentration, it deposits crystals of the complex nitrite,  $\text{Ru}_2\text{H}_2(\text{NO}_2)_4 \cdot 3\text{KNO}_2 + 4\text{H}_2\text{O}$ . This salt is very soluble in water, but almost insoluble in a concentrated solution of potassium chloride. It becomes anhydrous at  $100^\circ$ , but does not begin to decompose much below  $360^\circ$ ; at this temperature, however, decomposition is rapid. When heated with hydrochloric acid, it is rapidly reconverted into the double chloride from which it was formed.

C. H. B.

**Purification of Iridium.** By ÉMILE LEIDIÉ (*Compt. rend.*, 1899, 129, 214—215).—Iridium purified by fusion with lead is finely powdered, mixed with twice its weight of fused sodium chloride, and heated to incipient redness in a current of dry chlorine. The cooled product is treated with very dilute hydrochloric acid, and the filtered solution is heated to  $50$ — $60^\circ$ , and mixed with successive small quantities of sodium nitrite until the evolution of nitrogen oxides ceases and the liquid becomes neutral to litmus. It is then carefully mixed with sufficient sodium carbonate to make it alkaline to litmus, and with a slight excess of sodium nitrite, boiled for a few minutes, cooled and filtered; iron and gold are thus eliminated. A slight excess of sodium hydroxide is then added, and the solution, after cooling, is saturated with chlorine, heated gently, and treated with a rapid current of chlorine to eliminate ruthenium and osmium in the form of peroxides. The residual liquid is repeatedly evaporated with hydrochloric acid to decompose nitrites, nitrates, and chlorates, and the residue dissolved in cold chlorine water and crystallised to remove sodium chloride. The final crystalline separations are a mixture of sodium rutheniochloride and sodium iridiochloride; these are carefully dried, heated in dry chlorine at  $440^\circ$ , cooled, and treated with cold chlorine water. Ruthenium chloride remains undissolved, whilst the iridium passes into solution, and can be precipitated in the form of ammonium iridiochloride. The successful separation of iridium and ruthenium depends on obtaining the double chlorides free from any excess of sodium chloride, and on drying very carefully both the chlorine and the mixture of double chlorides.

C. H. B.

**Osmium.** By ARTHUR ROSENHEIM and EDWARD A. SASSERATH (*Zeit. anorg. Chem.*, 1899, 21, 122—144).—*Sodium sulphonosmate*,



is obtained by passing sulphurous anhydride through a solution of perosmic acid in 20 per cent. sodium hydroxide until this is nearly neutral to litmus, and then neutralising with a solution of sodium hydrogen sulphite. It crystallises in bright brown needles, is easily soluble in water at  $50^\circ$ , yielding a reddish-brown solution, which soon decomposes with precipitation of a black oxide. When treated with sodium hydroxide, it yields a violet solution of sodium osmate; with barium chloride, a bright brown barium salt, and with silver nitrate, a

yellowish-brown silver salt. The *potassium* salt,  $7\text{K}_2\text{O}, 4\text{OsO}_3, 10\text{SO}_2 + 7\text{H}_2\text{O}$ , obtained in a similar manner to the sodium salt, is more soluble in water than the latter, and can be recrystallised; decomposition takes place at  $70^\circ$ . It also crystallises with  $3\text{H}_2\text{O}$  and without water. If a stronger solution of potassium hydroxide is employed, a salt of the composition  $11\text{K}_2\text{O}, 4\text{OsO}_3, 14\text{SO}_2 + \text{H}_2\text{O}$  is obtained. Corresponding ammonium salts could not be prepared. Both the sodium and potassium salts are produced in almost theoretical quantities, and are very easily converted into other osmium salts. The sodium salt is also obtained by cautiously adding sodium hydrogen sulphite to a solution of sodium osmate, and since it yields sodium osmate when treated with sodium hydroxide and the corresponding barium and silver salts as described above, it probably has the constitution  $(\text{ONa})_2\text{Os}(\text{SO}_3\text{Na})_4 + 5\text{H}_2\text{O}$ . The potassium salt, which reacts in a similar manner, is probably derived from a salt of the composition  $\text{K}_2\text{OsO}_7$ .

Sodium osmium hexachloride,  $\text{Na}_6\text{OsCl}_{12}$ , obtained by gently heating sodium sulphonosmate in a current of hydrogen chloride, crystallises in lustrous leaflets, mixed with a small quantity of sodium hydrogen sulphite, cannot be recrystallised without decomposition, and when treated with potassium chloride is partially decomposed, forming the osmichloride,  $\text{K}_2\text{OsCl}_6$ . The corresponding potassium hexachloride is obtained by treating potassium sulphonosmate with hydrogen chloride.

Theoretical yields of the following compounds of quadrivalent osmium can be obtained from the sulphonosmates. Sodium osmichloride,  $\text{Na}_2\text{OsCl}_6 + 2\text{H}_2\text{O}$ , is formed by heating the sodium sulphonosmate in a current of hydrogen chloride, first at a gentle heat and finally at dull redness, and also by boiling it with excess of fuming hydrochloric acid (sp. gr. 1.19), then evaporating to dryness on the water-bath, extracting with absolute alcohol, and distilling the alcoholic solution under diminished pressure. The corresponding potassium and ammonium salts are described, those of the alkaline earths cannot be obtained by double decomposition from the sodium salt.

*Sodium osmibromide*,  $\text{Na}_2\text{OsBr}_6 + 4\text{H}_2\text{O}$ , obtained from the sulphonosmate by interaction with hydrogen bromide, crystallises in long, blackish-brown prisms having a metallic lustre. The *potassium* salt, a blackish-brown, crystalline powder having a copper-like lustre, crystallises from dilute solutions in large octahedra and is very sparingly soluble. The *ammonium* salt is a black, crystalline powder, soluble in water, and crystallises from dilute solutions in blackish-brown octahedra and tetrahedra. The *silver* salt is a flocculent, insoluble, indigo-blue precipitate.

Sodium sulphonosmate when treated with concentrated hydriodic acid, is completely decomposed with the formation of sulphurous anhydride, iodine, perosmic acid, and other products, and when gently heated in a current of dry hydrogen iodide, loses iodine and volatile osmium compounds, leaving a mixture of osmium tetroxide and iodine which can be separated mechanically. Complete decomposition also takes place with concentrated hydrofluoric acid, and a black precipitate of hydrated osmium dioxide,  $\text{OsO}_2 + 4\text{H}_2\text{O}$ , is obtained.

*Sodium osmisulphites*.—The salt  $[\text{Os}(\text{SO}_3)_6]\text{Na}_8 + 8\text{H}_2\text{O}$  is obtained by boiling an aqueous solution of sodium osmichloride with concen-

trated sodium hydrogen sulphite for some time. It crystallises from dilute sodium hydrogen sulphite in microscopic, brownish-white prisms, is sparingly soluble in water, and decomposes with a bluish-green coloration, gives an intense blue precipitate when treated with alkali, and does not yield all its sulphurous acid when boiled with concentrated hydrochloric acid. It is also obtained with  $3\text{H}_2\text{O}$  by leaving a mixture of sodium sulphonosmate and sodium hydrogen sulphite in a closed flask for some weeks. The salt  $[\text{Os}(\text{H}_2\text{O})(\text{SO}_3)_5]\text{Na}_6 + 4\text{H}_2\text{O}$ , obtained by boiling sodium sulphonosmate with sodium hydrogen sulphite, is a white, crystalline powder. The salt  $[\text{OsCl}(\text{SO}_3)_5]\text{Na}_7 + 6\text{H}_2\text{O}$ , prepared by heating sodium osmichloride with a solution of sodium sulphite at  $60^\circ$ , is a bright violet, crystalline powder, which dissolves in boiling water with a reddish-violet coloration and then decomposes, yielding a violet precipitate. The chlorine in this compound cannot be precipitated quantitatively with silver nitrate. The salt  $[\text{OsO}(\text{SO}_3)_4]\text{Na}_6 + 3\text{H}_2\text{O}$ , obtained by the action of sodium sulphite on sodium sulphonosmate at  $50^\circ$ , is a deep violet, crystalline precipitate.

*Potassium osmisulphites*,  $[\text{Os}(\text{SO}_3)_6]\text{K}_6\text{H}_2 + 2\text{H}_2\text{O}$ , obtained by boiling a solution of potassium sulphonosmate with potassium hydrogen sulphite, crystallises in beautiful, white needles, is more easily soluble than the sodium salts, and can be recrystallised from water without decomposition. It is also obtained by boiling potassium osmitetrachloride with potassium hydrogen sulphite and by allowing a mixture of potassium sulphonosmate and potassium hydrogen sulphite to remain at the ordinary temperature. The salt  $[\text{Os}(\text{H}_2\text{O})(\text{SO}_3)_5]\text{K}_6 + 4\text{H}_2\text{O}$  is obtained, together with a small quantity of a salt containing chlorine, by adding potassium sulphite to a cold solution of potassium osmichloride; it crystallises in white needles. The chlorine compound forms long, yellow needles. The salt  $[\text{Os}(\text{H}_2\text{O})(\text{SO}_3)_{11}]\text{K}_{11}\text{H}_3 + 5\text{H}_2\text{O}$ , obtained by the action of potassium hydrogen sulphite on potassium sulphonosmate in the cold or at a gentle heat, is a beautiful, white or pale rose compound, and can be recrystallised without decomposition.

E. C. R.

### Mineralogical Chemistry.

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Occurrence of Vanadium, Chromium, and Titanium in Peats. By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1899, 21, 706—707).—Small quantities of these three elements have been found in the ashes from three different samples of peat from Hyde Swamps, near the northern junction of Beaufort and Hyde Counties, North Carolina.  
J. J. S.

Copper Glance pseudomorphous after Copper Pyrites from the Altai Mountains. By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1899, 31, 508; from *Bull. Acad. Sci. St. Pétersbourg*, 1897, [v], 6, xxxvii—xxxix).—Quartz veins near the Georgieff gold washings on the rivers Berdj and Kamenka contain copper glance in lamellar masses,

copper pyrites, hæmatite, chrysocolla and malachite. All these minerals have been derived from the copper pyrites, and all stages of passage from copper pyrites to copper glance can be seen. Analysis by J. A. Antipoff of the copper glance gave :

Cu.	S.	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CO <sub>2</sub> .	Sb.	As.	CaO.	Total.
68·76	17·12	2·44	1·33	6·32	0·82	trace	1·03	97·82
L. J. S.								

**Cinnabar Ores in Servia.** By J. Z. RAUŠAR (*Zeit. Kryst. Min.*, 1899, 31, 525; from *Zeit. chem. Industrie, Prag.*, 1896, 52—54).—Besides being found at the abandoned works of Avala, cinnabar occurs near Šabac as a crust on lead ores. The galena contains Pb, 55·51; Hg, 0·229; Ag, 0·01 per cent. L. J. S.

**Thallium in Marcasite from Poland.** By J. A. ANTIPOFF (*Zeit. Kryst. Min.*, 1899, 31, 515; from *J. Russ. Chem. Soc.*, 1896, 28, 384—387).—Analysis gave :

Fe.	S.	As.	Tl.	SiO <sub>2</sub> .	Zn.	Total.
47·831	44·772	0·783	0·311	2·840	trace	96·537

A second determination of the thallium gave 0·532. The difference (3·463 per cent.) is probably oxygen. This is the largest amount of thallium that has been noted in a pyrites-like mineral. The above analysis corrects that previously given (this vol., ii, 109).

L. J. S.

**Cupro-goslarite, a New Variety of Zinc Sulphate.** By AUSTIN F. ROGERS (*Kansas Univ. Quart.*, 1899, 8, A, 105—106).—A translucent, greenish-blue incrustation on the walls of an abandoned zinc mine at Galena, Cherokee Co., Kansas, gave the following results on analysis. It has doubtless been formed by the oxidation of the blende and copper pyrites which occur in the mine. On exposure to the air, it loses some water and becomes white. Analysis gave :

ZnO.	CuO.	FeO.	H <sub>2</sub> O.	SO <sub>3</sub> .	Insol.	Total.
23·83	6·68	0·13	41·76	[27·02]	0·58	100·00

This amount of copper oxide corresponds with 12·48 per cent. of copper sulphate in the mineral. The percentage of water is calculated from the loss at 100°, on the assumption that six-sevenths of the water was expelled at that temperature. L. J. S.

**Spinel and Forsterite from the Glenelg Limestone (Inverness-shire).** By CHARLES THOMAS CLOUGH and WILLIAM POLLARD (*Quart. Journ. Geol. Soc.*, 1899, 55, 372—380).—The limestone bands occurring in the gneisses and schists (probably of sedimentary origin) on the southern side of the Big Glen, or Glenmore, of Glenelg, contain a variety of minerals, including white diopside in large masses, a serpentinous mineral, phlogopite, graphite, tremolite, a dark hornblende, and quartz. The serpentine is sometimes seen to be derived from a colourless olivine, which is shown by analysis I to be forsterite. Lumps in the limestone consisting mainly of forsterite contain grains 2—5 mm. across of pale blue spinel (analysis II). Dark green octahedra of spinel and a violet spinel also occur.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO.	CaO.	MnO.	MgO.	Loss on ignition.	Total.	Sp. gr.
I.	41.16	1.02	2.00	0.26	0.26	54.86	0.70	100.26	3.24
II.	1.20	69.80	2.03	—	—	27.30	—	100.33	3.57

The forsterite also contains traces of titanium oxide and fluorine. This association of minerals is the same as that in the metamorphic limestone of Passau in Bavaria (Abstr., 1897, ii, 413). L. J. S.

**Ilmenite from Russia.** By FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1899, 31, 525; from *Rozpravy České Akad. [Memoirs Bohemian Acad.]*, 1896, 5, Class II, No. XXXVII., 3 pp.).—The sand of a small lake in the granite district at Stepanowka, near Voronovica, Gov. Podolien, contains about a quarter per cent. of a black, granular mineral with metallic lustre and conchoidal fracture. Sp. gr. 4.543; only a few grains are attracted by the magnet. Analyses gave:

TiO <sub>2</sub>	FeO.	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO.	MgO.	Total.
50.85	42.55	2.23	3.67	0.12	0.18	trace	99.60
51.20	43.04	2.06	2.98	0.20	0.14	trace	99.62

Deducting SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO, these analyses give the formula 44FeTiO<sub>3</sub>, Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>. L. J. S.

**Analyses of Bohemian Minerals.** By KARL PREIS (*Zeit. Kryst. Min.*, 1899, 31, 526; from *Sitz.-ber. k. böhm. Ges. d. Wiss.*, 1897, No. XIX., 5 pp.).—*Monazite* from Pisek gave:

P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	Ce <sub>2</sub> O <sub>3</sub>	(La, Di) <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO.	H <sub>2</sub> O.	Insol.	Total.
27.57	1.46	31.05	26.64	4.02	5.85	1.32	0.41	0.42	1.96	100.70

There is no simple relation between the amounts of silica and thorium, so they are probably not present as thorite.

*Phenakite* from Ober-Neusattel gave: SiO<sub>2</sub>, 54.27; BeO, 45.17; H<sub>2</sub>O, 0.53 = 99.98.

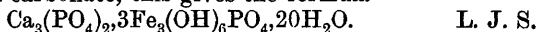
*Damourite*, from the primitive limestone at Tabor, gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
43.69	39.57	1.02	0.60	9.98	0.90	4.97	100.73

*Delvauxite* occurs at Trpin, near Beraun, in lenticular nodules with wrinkled surfaces, and, in the interior, of a brown colour. Analysis by E. Butta gave:

P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO.	CO <sub>2</sub>	H <sub>2</sub> O.	Insol.
18.45	38.74	2.71	9.63	1.38	26.22	3.95

Deducting calcium carbonate, this gives the formula



L. J. S.

**A New Cerium Mineral from the Caucasus.** By G. TSCHERNIK (*Zeit. Kryst. Min.*, 1899, 31, 513; from *J. Russ. Chem. Soc.*, 1896, 28, 345—359).—A pebble from Gov. Batum, South Caucasus, consists of an opaque, black mineral, with greasy lustre and white streak. It is very brittle, and has an uneven to splintery fracture. H = 5—6; sp. gr. 5.08. It encloses small crystals of copper pyrites. The mean of three closely agreeing analyses made on material from different parts of the pebble is:

SiO <sub>2</sub> .	CeO.	LaO.	DiO.	YO.	ErO.	ZrO <sub>2</sub> .	TiO <sub>2</sub> .	ThO <sub>2</sub> .
6·57	34·20	6·73	2·27	6·97	0·67	11·67	14·73	0·73
	UO.	CaO.	FeO.	CuO.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	H <sub>2</sub> O.	
	0·03	2·33	3·70	0·67	3·30	0·97	3·43	

A pebble of wolframite from the river Tschoroch, near the town Batum, gave :

WO <sub>3</sub> .	MoO <sub>3</sub> .	SnO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	Total.	Sp. gr.
74·1	1·6	5·1	17·5	1·3	99·6	7·53

L. J. S.

**Argon and Helium in Cerium Minerals from the Caucasus.** By G. TSCHERNIK (*Zeit. Kryst. Min.*, 1899, 31, 514; from *J. Russ. Chem. Soc.*, 1897, 29, 291—302).—Analysis of gas from the cerium mineral from the Caucasus (preceding abstract) gave: O, 4·8; H, 3·6; N + argon, 90·5 = 98·9.

Analysis of the ash of coal from Tkwibuli, near Kutais, gave approximately :

Helium.	CeO.	LaO.	DiO.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaSO <sub>4</sub> .
1·1	3·86	3·71	2·34	18·0	11·0	52·0

It also contains Fe, Mg, Mn, K, Na, Y.

L. J. S.

**Loranskite, a New Mineral.** By MICHAEL P. MELNIKOFF (*Zeit. Kryst. Min.*, 1899, 31, 505; from separate publication, *St. Petersburg*).—Loranskite is a massive, black mineral from the quartz-veins at Imbilax, near Pitkäranta, Finland. It is brittle, and has a conchoidal fracture; strong sub-metallic lustre; H = 5; sp. gr. about 4·6. Streak, greenish-grey. On the edges it is translucent and greenish-yellow; optically isotropic.

L. J. S.

**Analysis of Loranskite.** By PETR D. NIKOLAEFF (*Zeit. Kryst. Min.*, 1899, 31, 505; from *Verh. k. russ. min. Ges.*, 1897, [ii], 35, Protokolle, 11—13. Compare preceding abstract).—A preliminary analysis gave :

Ta <sub>2</sub> O <sub>5</sub> .	Y earths.	CeO.	CaO.	Fe <sub>2</sub> O <sub>3</sub> .	ZrO <sub>2</sub> .	Loss on ignition.	Total.	Sp. gr.
47·00	10·00	3·00	3·30	4·00	20·00	8·15	95·45	4·162

Also some sulphur, titanium and manganese. Rare earths showing an absorption spectrum are absent. The mineral is only slightly attacked by acids or by fusing with alkalis. It is completely decomposed by fusing with potassium fluoride.

L. J. S.

**Aluminium Phosphate from Moravia.** By FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1899, 31, 525; from *Rozpravy České Akad. [Memoirs Bohemian Acad.]*, 1896, 5, class II, No. XV (II), 7 pp.).—On the walls of crevices in ochreous limonite from Gross-Tresny near Oels, are drusy spheres, with an internal radial structure of a light grey mineral. At first it is translucent, but on exposure to the air it becomes dull and opaque. Fresh pure material has sp. gr. 2·617; H = 4. Analyses gave :

Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	MnO.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Insol.	Total.
42·28	0·98	0·56	0·42	trace	29·01	26·86	0·25	100·36
42·17	1·04	0·49	0·30	trace	28·94	26·93	0·34	100·21



At 100°, there is a loss of 10·32, and at 200°, of 16·55 per cent. of water, the remainder being expelled only at a red heat. In composition, the mineral comes between peganite and fischerite, and agrees best with sphærite.

L. J. S.

**Analyses of Phosphates from New South Wales.** By JOHN C. H. MINGAYE (*Rept. Australian Assoc.*, 1898, 7, 332—333; and *Records Geol. Survey N.S. Wales*, 1899, 6, 116—118).—Pyromorphite from Braidwood, near Little River, gave :

PbO.	Pb.	P <sub>2</sub> O <sub>5</sub> .	V <sub>2</sub> O <sub>5</sub> .	Cl.	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Insol.	Total.
69·40	6·57	15·22	trace	2·26	0·62	trace	0·86	4·67	99·60

Partial analyses are also given of apatite (*Abstr.*, 1898, ii, 386), marsupial excrement, phosphatic deposits from Moruya Caves, and of gem gravels containing zircon and phosphates of the rare earths.

L. J. S.

**Phosphatic Deposits in the Jenolan Caves, N. S. Wales.** By JOHN C. H. MINGAYE (*Rept. Australian Assoc.*, 1898, 7, 327—331; and *Records Geol. Survey N.S. Wales*, 1899, 6, 111—116).—The large and numerous Jenolan caves are in a thick bed of Siluro-Devonian limestone. The following analyses are given of materials from the caves :

I. Reddish marl, which partly fills portions of the caves ; it also contains MnO, trace, and organic matter, 0·24 per cent.

II and III. Light, porous, white substance, occurring as veins in the white and red marls ; it is soluble in dilute hydrochloric acid. Trace of chlorine in II.

IV and V. A deposit under a layer of gypsum on the floor of the cave. Contains also traces of chlorine, and, in IV, SO<sub>3</sub>, 5·39 ; in V, SO<sub>3</sub>, 28·67 per cent.

VI. Light, fluffy, fungoid substance on the walls ; it resembles very light wadding, and is easily blown about. Contains also CaCO<sub>3</sub>, 76·03 ; MgCO<sub>3</sub>, 6·12 ; SrCO<sub>3</sub>, trace, and organic matter, 1·32 per cent.

VII. Same as VI. Contains also CaCO<sub>3</sub>, 72·57 ; MgCO<sub>3</sub>, 5·28 ; SrCO<sub>3</sub>, trace, and organic matter, 1·14 per cent.

VIII. A nodular, grey substance.

	H <sub>2</sub> O.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	CO <sub>2</sub> .	Total.
I.	4·50	63·41	18·02	7·33	0·16	0·79	5·09	trace	0·08	—	99·62
II.	33·60	0·70	26·83	0·72	8·10	0·14	0·09	nil	30·04	0·15	100·37
III.	9·83	50·10	13·88	8·65	1·02	0·14	1·35	trace	15·38	0·12	100·47
IV.	16·82	37·82	0·64	trace	22·66	0·32	0·11	—	15·71	0·24	99·71
V.	22·59	2·78	0·10	nil	31·52	0·09	trace	—	14·50	0·10	100·35
VI.	1·88	13·22	1·46	—	—	—	—	—	0·28	—	100·31
VII.	1·48	17·26	1·94	—	—	—	—	—	trace	—	99·67
VIII.	10·31	54·13	15·13	7·46	nil	trace	1·69	0·87	10·63	—	100·22

Minervite also occurs in the caves (*Abstr.*, 1898, ii, 386).

Nitre, as a white efflorescence from crevices, contains small quantities of lime, magnesia, chlorine and sulphuric acid.

Bat guano and bone breccias are not associated with these substances.

The phosphoric acid has doubtless been derived from bones, and in acting on the marls has given rise to potassium and aluminium phosphates (compare *Abstr.*, 1896, ii, 185).

L. J. S.

**Garnet from the Urals.** By V. VON WOROBIEFF (*Zeit. Kryst. Min.*, 1899, 31, 504; from *Verh. k. russ. min. Ges.*, 1897, 35, 19—42).—The optical characters of garnets from the Eugenie-Maximilianoff mines are described; they are in agreement with those described by Karnojitsky from the same locality (this vol., ii, 37). The yellow dodecahedral crystals show well-marked optical anomalies, and the optical orientation varies in zones of different colour. The author considers garnet to be pseudo-cubic, and the twin-lamellæ to be the result of paramorphic strains. Analyses of hessonite gave:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Total.
39·3	0·4	6·3	17·9	35·5	1·3	100·7
39·5	0·2	6·2	17·6	34·5	1·8	99·8

L. J. S.

**Garnet pseudomorphous after Idocrase from the Urals.** By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1899, 31, 505; from *Verh. k. russ. min. Ges.*, 1897, [ii], 35, Protokolle, 14—16).—Pebbles and fragments with parting planes, and pyramidal crystals with the forms of idocrase, are found in the gold washings on the Borsowka river, near Kyschtysk; they consist of a microcrystalline aggregate of garnet. Analysis by P. Nikolaëff gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Loss on ignition.	Total.
36·58	18·67	4·33	35·57	3·48	0·75	99·38

The idocrase has here been altered to pure garnet without being intermixed with clinocllore, diopside, &c. L. J. S.

**Fibrous Forms of Silica from Moravian Serpentine.** By JINDŘICH LADISLAV BARVÍK (*Zeit. Kryst. Min.*, 1899, 31, 525; from *Sitz.ber. k. böhm. Ges. d. Wiss.*, 1897, No. XIV, 8 pp.).—By their optical characters, quartzine, chalcedony, lutecite and lussatite are identified from the quartzose veins in Moravian serpentine. Lussatite from Ratkowic is white and fibrous, and occurs mixed with opal, from which it has probably been derived. Sp. gr. 2·015. Analysis gave: SiO<sub>2</sub>, 90·64, loss on ignition, 2·62 per cent.; also MgO, FeO and Al<sub>2</sub>O<sub>3</sub>. L. J. S.

**Minerals from Moravia.** By FRANTIŠEK KOVÁŘ (*Zeit. Kryst. Min.*, 1899, 31, 523—525; from *Rozpravy České Akad. [Memoirs Bohemian Acad.]*, 1896, 5, Class II, No. XV (I), 18 pp.).—The minerals described are from the graphite mines of Gross-Tresny.

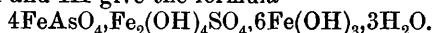
*Stolpenite* fills crevices in the limestone which carries the graphite. It is earthy and compact with a greasy lustre, and is brown on the surface, but siskin-green on a fresh fracture. It crumbles slowly in water. Sp. gr. 2·365. Analyses I and II. 7·95 per cent. of the water is only expelled at a red heat, hence the formula  $H_4CaAl_4Si_3O_{27} + 15H_2O$ .

*Nontronite* forms a sulphur-yellow incrustation on graphite. Sp. gr. 2·145. Analyses III and IV give the formula  $Fe_2Si_3O_9 + 5H_2O$ .

*Kaolinite* occurs with graphite in limonite, limestone and hæmatite. Analyses V—VII of white material; in VI and VII there are traces of CO<sub>2</sub>, and in VII also P<sub>2</sub>O<sub>5</sub>.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	(K,Na) <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	48·50	—	18·90	0·42	5·12	0·13	—	27·40	100·47
II.	48·37	—	19·48	—	4·98	0·19	—	27·49	100·51
III.	41·78	—	35·30	0·86	0·92	0·40	—	20·68	99·94
IV.	41·65	—	36·24	—	1·01	0·37	—	20·74	100·01
V.	46·02	0·18	37·85	0·47	0·68	0·35	1·06	13·70	100·31
VI.	48·65	0·39	35·18	0·76	0·73	0·46	0·93	12·82	99·92
VII.	53·15	0·92	30·05	1·66	0·64	0·49	1·40	12·25	100·56

*Patticite* occurs as stalactites in a shaft through limestone containing much mispickel. The stalactites attain a length of 10 cm., and consist of alternate shells of soft, yellow, and of hard, brown materials. Analyses VIII and IX give the formula



*Evansite* occurs on limonite as a botryoidal coating of a white (analysis X), or of a yellowish colour (analysis XI). The analyses (traces of magnesia are also present) agree with those required for the usual formula  $\text{AlPO}_4, 2\text{Al}(\text{OH})_3, 6\text{H}_2\text{O}$ .

	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	As <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	H <sub>2</sub> O.	Insol.	Total.	Sp. gr.
VIII.	—	55·06	trace	26·13	—	4·64	14·29	0·12	100·24	2·475
IX.	—	55·19	trace	25·91	—	4·49	14·48	0·23	100·30	2·489
X.	39·22	0·87	0·41	—	18·02	—	41·47	0·15	100·14	1·874
XI.	38·05	1·92	0·23	—	18·48	—	41·29	0·44	100·41	1·937

L. J. S.

**Analcite from Baku, Caucasus.** By KONSTANTIN D. GLINKA (*Zeit. Kryst. Min.*, 1899, 31, 517; from *Travaux Soc. Nat. Varsovie, Compt. rend., section phys. et chim.*, 1895–1896, No. 3).—A rock fragment from the blue clay of a mud volcano near Baku consists of pyroxene, a brown, isotropic substance, quartz and magnetite, together with analcite, which occurs either as a constituent of the rock or in cavities with celadonite. The analcite crystals are colourless and transparent, and are bounded by perfect faces of the form {211}; sections parallel to (100) are birefringent. The results of the analysis agree with those required for the usual formula  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$ .

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
55·19	22·84	13·44	8·60	100·07

L. J. S.

**Jadeite and Széchenyiite from Burma.** By JÓZSEF A. KRENNER (*Zeit. Kryst. Min.*, 1899, 31, 502–504; from *Scientific Results of Count Béla Széchenyi's Journey in Eastern Asia*, 1877–1880, Budapest, 1897, 3, 285–291, Hungarian).—Most of the specimens were bought in the market at Bhamo; the jadeite is usually white or greenish-white, but also pale grass-green and leek-green, and sometimes with emerald-green spots. The surfaces of the pebbles and fragments have a weathered crust, 1–10 mm. thick, which is either brown and compact, or light tile-red, and non-coherent. In thin sections, the larger, colourless fibres (1 × 10 mm.) show the optical characters of a monoclinic pyroxene. The prism cleavage angle = 93° 5'; optically

positive,  $Bx \wedge c' = 33^\circ 34'$ ,  $2V = 71^\circ 56'$ ,  $\beta = 1.654$  (Na). Analysis by J. Loczka gave the results under I, agreeing with those required for the formula  $NaAl(SiO_3)_2$ . The emerald-green spots contain a little iron and traces of chromium.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	59.77	24.10	0.54	—	0.29	0.62	0.17	13.61	0.36	99.46	3.323
II.	55.02	4.53	1.04	3.28	20.36	8.00	1.52	6.71	0.51	100.97	3.033

*Széchenyiite* is the name given to a dark brownish-green, foliated mineral embedded in greenish jadeite; it resembles diallage in appearance, but is shown to have the characters of an amphibole. The fibres have a prism cleavage angle of  $56^\circ 8'$ , and an extinction angle on (010) of  $16^\circ 16'$ ; the pleochroism is feeble. Splinters easily fuse and give a strong yellow coloration to the flame. Analysis by J. Loczka gave II, agreeing with  $2Na_2O, 10MgO, 3CaO, Al_2O_3, 16SiO_2$ . In some of the jadeite specimens are light greenish-yellow or colourless fibres of amphibole. This occurrence of amphibole explains the presence of magnesia and lime shown in some analyses of jadeite.

L. J. S.

**Auerbachite, and the Rock in which it occurs.** By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1899, 31, 512; from *Bull. Acad. Sci. St. Pétersbourg*, 1897, 7, 89—95).—An examination of auerbachite from near Mariupol, Gov. Ekaterinoslaff, shows that the mineral in its chemical, physical and geometric characters is identical with zircon. The excess of silica is due to the large numbers of enclosed ægirite needles. The crystals are sometimes altered to a white, porous material resembling porcelain.

The rock in which auerbachite occurs is shown not to be a quartzschist, but to be a pure, schist-like aggregate of albite crystals with a few small ægirite crystals. Analysis gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO, K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss on ignition.	Total.
60.29	21.39	3.07	0.46	traces	12.30	0.67	98.18

L. J. S.

**Microcline pseudomorphous after Adularia from the Altai Mountains.** By PAVEL V. VON JEREMÉEFF (*Zeit. Kryst. Min.*, 1899, 31, 506; from *Verh. k. russ. min. Ges.*, 1897, [ii], 35, Protokolle, 55—56).—The pseudo-crystals have bright, smooth faces, and are twinned according to the Manebach and Baveno laws; they consist of an aggregate of microcline individuals. Analysis by P. Nikolaéeff gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO, MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss on ignition.	Total.
63.41	18.60	0.57	traces	10.09	6.01	0.54	99.22

L. J. S.

**Clay from Russia.** By WLADIMIR ALEXÉEFF (*Zeit. Kryst. Min.*, 1899, 31, 509; from *Verh. k. russ. min. Ges.*, 1897, [ii], 35, Protokolle, 63).—A clay from Kossoi Brod on the Chusovaya (Tschusowaja) river, Perm, is seen, under the microscope, to consist of

irregular, transparent, and birefringent lamellæ. Analysis shows it to be near pyrophyllite. It contains 38·6 per cent. of quartz.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
67·60	22·22	1·65	0·18	0·28	3·93	5·37	101·23
L. J. S.							

**Rock Analyses.** By EDMOND BONJEAN (*Bull. Soc. Chim.*, 1899, [iii], 21, 691—693).—Details of work already published (this vol., ii, 500).  
N. L.

**Meteorite from Zavid.** By CARL HÖDLMOSEK (*Tsch. Min. Mitth.*, 1899, 18, 513—517).—The bulk analysis of the stone which fell at Zavid, in Bosnia, gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe.	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	S.	Total less O for S.
41·90	1·92	0·15	27·40	4·60	22·79	1·05	0·41	0·39	1·01	101·11

Also traces of cobalt, nickel and manganese. Sp. gr. 3·5241. The metallic iron was estimated from the amount of hydrogen liberated when the material was treated with acid; a description and figure are given of the apparatus used in the estimation.  
L. J. S.

**Analysis of Meteoric Iron.** By O. SJÖSTRÖM (*Mitth. naturwiss. Ver. f. Neu-Vorpommern u. Rügen*, 1899, 30, 1—29).—The author gives the details of the methods of separation and estimation used by him in the analysis of meteoric irons. The methods are essentially the same as those outlined by Cohen (*Abstr.*, 1893, ii, 20), and several of the author's analyses are given in recent papers by Cohen.  
L. J. S.

**Meteoric Irons.** By EMIL W. COHEN (*Ann. k.k. naturhist. Hofmus. Wien*, 1899, 13, 473—486).—A review of the literature and notes concerning the structure are given of various meteoric irons; the following new analyses by O. Sjöström are given:

*Shingle Springs*, El Dorado Co., California.—In the large proportion of nickel and in the bright etching spots, this resembles the Cape of Good Hope, Iquique, and Kokomo irons (this vol., ii, 307). Sp. gr. 7·8943. Analysis gave the results under I, corresponding with the following mineralogical composition: Nickel-iron, 97·65; nickel-iron phosphides, 2·21; troilite, 0·14.

*Magura*, Hungary.—The angular fragments left after dissolving the iron in very dilute hydrochloric acid gave, on analysis, the results under II. As in other irons, this material consists mainly of kamacite, with perhaps a little tænite.

	Fe.	Ni.	Co.	Cu.	Cr.	C.	P.	S.	Total.
I.	82·21	16·69	0·65	0·02	0·02	0·03	0·34	0·05	100·01
II.	92·54	6·40	0·73	—	—	0·00	0·09	—	99·76

Previous analyses (*Abstr.*, 1893, ii, 20) of tænite (a nickel-iron) show the presence of small amounts of carbon. New determinations made on tænite from the Toluca and Glorieta Mt. irons gave 0·22 and 0·12 per cent. of carbon respectively.  
L. J. S.

**Red Rain Dust.** By THOMAS STEEL (*Rept. Australian Assoc.*, 1898, 7, 334—335).—On December 27th, 1896, there occurred over Mel-

bourne and a considerable area of Victoria an unusually heavy fall of dust of a red colour, which was carried down by accompanying rain. Analysis of this dust (dried at 110°) gave:

Soluble						Insol.	Loss on
SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	SO <sub>3</sub> .	and diff.	ignition.
0·75	4·68	0·50	15·16	1·36	0·62	[66·23]	10·70

The loss on ignition includes: H<sub>2</sub>O, 6·08; N, 0·30, and organic matter. This composition agrees with that of an ordinary surface soil derived from volcanic rocks. Under the microscope, diatoms, lepidopterous scales, quartz, and garnet have been detected in the material.

L. J. S.

**Mineral Waters of Mont Dore.** By F. PARMENTIER (*Compt. rend.*, 1899, 128, 1408—1409).—Mineral waters from neighbouring springs generally contain the same constituents, but the water taken from borings in the neighbourhood of Mont Dore presents no points of similarity with samples obtained from other sources in the same district. It contains a comparatively large amount of sodium chloride and notable quantities of sodium arsenate, iron being entirely absent.

G. T. M.

**Mineral Waters containing Fluorine.** By F. PARMENTIER (*Compt. rend.*, 1899, 128, 1409—1410).—In reply to Lepierre (this vol., ii, 602), the author states that his remarks on the occurrence of fluorides in mineral waters refer to the special case of water from Mont Dore and St. Honoré-les-Bains (compare this vol., ii, 501).

G. T. M.

**Analysis of Waters from the Tougourt-Ouargla District of the Sahara Desert.** By E. LAHACHE (*J. Pharm.*, 1899, [vi], 9, 477—482).—Analyses of water from the following places in the Sahara:—Tougourt, Bled et Amax, El-Fetir, H. Messaoud, El-Hadjira, H. Dahane, H. Debiche et Strifigi, Donionidi, N'Gonça, Ouargla.

H. R. LE S.

## Physiological Chemistry.

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**The Effect of Compression of one Lung on the Respiratory Gas Exchange.** By VAUGHAN HARLEY (*J. Physiol.*, 1899, 25, 33—48). —The experiments were made on dogs, morphine being administered to prevent muscular action. The compression of one lung (right or left) is followed by an increased rate of breathing as a rule, and always by an increase in the quantity of air breathed, of oxygen absorbed, and of carbonic anhydride eliminated; the respiratory quotient is, as a rule, not altered.

The cause of the increase in gas exchange is not due to the increased rate of breathing, for the latter did not always occur; nor is it due to an increase of body temperature, or to displacement of the heart. A

possible explanation is, that carbonic anhydride is a secretion of the alveolar epithelium (Bohr), and that carbonic anhydride acts as a stimulant to its own secretion.

W. D. H.

**Pancreatic Diabetes.** By IVOR LL. TUCKETT (*J. Physiol.*, 1899, 25, 63—68).—Gaglio found that extirpation of the pancreas was not followed by glycosuria if the thoracic duct was ligatured. This, if true, proves that something enters the circulation by the thoracic lymph which normally is destroyed by the pancreas, and which, in the absence of the pancreas, causes glycosuria. But Lepine and Biedl maintain that ligature of the thoracic duct increases the glycosuria caused by excision of the pancreas. Ligature or fistula of the left thoracic duct in dogs is in itself a cause of glycosuria (Biedl). The present communication is a preliminary account of experiments which support the following supposition, and so reconcile the above opposing statements:—Glycosuria, which follows interference with the thoracic duct, is but a mild form of pancreatic diabetes, if we assume that the pancreas has an internal secretion ( $t$ ) which enters the circulation constantly *via* the thoracic lymph; and also that a toxic substance ( $t'$ ) capable of causing glycosuria, if not neutralised by  $t$ , is absorbed from the intestine during digestion *via* the lymph stream. It must also be assumed that the thoracic lymph contains a large quantity of  $t'$  during digestion, but none at other times, whereas only a small quantity of  $t$  is ever present in the thoracic lymph, but the blood always contains a relatively large quantity, as it is continually accumulating there.

If the thoracic lymph from a fasting animal is injected into the portal circulation of another animal, there is no hyperglycæmia or glycosuria; but if the lymph injected be from a digesting animal, the hypothetical  $t'$  acts on the liver cells deleteriously and produces hyperglycæmia and glycosuria. If the lymph is injected into the general blood stream, the effect is less marked, namely,  $t'$  is then partially neutralised by  $t$  before it acts on the liver. If the venous return from the pancreas is impeded by air bubbles, the secretion of  $t$  is checked, and glycosuria is more marked.

W. D. H.

**The Behaviour of Benzoyl Peroxide and Calcium Peroxide in the Digestive Canal of Dogs and Men.** By MARCELLUS NENCKI and J. ZALESKI (*Zeit. physiol. Chem.*, 1899, 27, 487—506).—The administration of such drugs as calomel and castor oil was empirical previous to the discovery of the true nature of putrefaction. The absolute disinfection of the alimentary canal is not possible, or even advisable; the use of antiseptics is limited because of their harmful effects on the alimentary canal. After the discovery that pancreatic juice will decompose, not only fats, but also many salts of the aromatic series, into their components, the use of such substances as salol (which is resolved into salicylic acid and phenol) became possible. The present research relates to the use of oxygen, not in the free state, but by the decomposition of peroxides. The use of organic peroxides dates from the time of Brodie (1863). Benzoyl peroxide is undoubtedly decomposed in the intestine; hippuric acid appears in the urine, although not in amount sufficient to account for half of the drug given. Experiments with artificial digestion confirmed this; but the drug has



little or no effect on the amount of ethereal hydrogen sulphates in the urine. Better results followed the use of calcium peroxide; it appears to be more readily decomposed; it has no harmful effects; in dogs, the ethereal hydrogen sulphates are lessened, and the indican completely disappears; its effect is transitory; in man, especially in the acid dyspepsia of children, it is beneficial. W. D. H.

**Physiological Effects of 'Peptone' when Injected into the Circulation.** By WILLIAM H. THOMPSON (*J. Physiol.*, 1899, 25, 1—21).—This is a continuation of results already published (this vol., ii, 604), and relates to the influence of the constituents of 'peptone' on the vessels of the spleen, liver, and limbs, all of which were investigated by the plethysmographic method. The vessels of the spleen share, to a moderate extent, the dilatation which produces the fall of blood pressure. Vaso-mobility, as tested by stimulation of the splanchnic nerves, is diminished, but to a less degree than in the intestinal, although in a greater degree than in the renal, district. The vessels of the liver are enormously dilated, the accumulation of blood there exceeding that in the intestines. The liver, in fact, probably plays the part of a safety receptacle to the heart. There is also a great depression of vaso-mobility. The effect on the limb-vessels is very slight, even less than on those of the kidneys.

Of the constituents of Witte's peptone, proto- and hetero-proteose are the most effective in producing these results. Deuteroproteose and purified peptone have comparatively little influence.

W. D. H.

**The Effects on Blood and Urine of the Intravenous and Subcutaneous Injection of Various Carbohydrates.** By FREDERICK W. PAVY (*J. Physiol.*, 1899, 24, 479—517).—The sugar normally present in blood does not consist exclusively of dextrose, its reducing power compared with that of dextrose being 75 : 100. The small amount of sugar in normal urine has an even smaller reducing power. The amount of sugar found in the blood collected immediately after the injection of large doses (in rabbits) is greater in the case of the saccharoses than in that of the hexoses. The highest figures (21—24 per 1000) occur after cane sugar; galactose and dextrose give respectively 11—12 and 14—15 per 1000. After small doses, the same disparity is not observable. The saccharoses comport themselves as unserviceable foreign matter and are speedily cast out into the urine. The results obtained with maltose are ambiguous; after intravenous injection, they correspond with those of lactose and cane sugar; after subcutaneous injection, the results correspond with those of the hexoses. The hexoses show a low degree of elimination; galactose escapes more freely than lævulose or dextrose, between which there is not much difference. Dextrose appears to undergo an alteration; after injecting a large quantity, it is found in both blood and urine; injected in less quantity, the reducing power of the sugar in the blood and still more of the sugar in the urine is far less than that of dextrose. In the case of galactose, and probably also in that of lævulose, there is no such change.

Glycogen injected intravenously causes a rise of sugar in the blood,

and the elimination in the urine of a considerable amount of a product with low reducing power.

Considerable stress is laid on the generalisation that the sugars susceptible of application by the body are those which ferment with yeast; a sugar which yeast can appropriate is likewise susceptible of appropriation by living matter of another kind, not necessarily that of the liver exclusively, but by the protoplasmic matter of the body generally.

W. D. H.

**Elimination of Nitrogen and Phosphorus during Assimilation.** By WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1899, 129, 223—224).—Observations made in 1892 and 1893 on infants fed on milk show that the ratio of phosphoric anhydride to nitrogen,  $N/P_2O_5$ , in the urine varies from 1/5.2 to 1/10.4, and the results are practically identical with those recently described by Keller.

C. H. B.

**Further Proofs of the Origin of Uric Acid from Nuclein Compounds and Derivatives.** By WILLIAM J. SMITH JEROME (*J. Physiol.*, 1899, 25, 98—104).—Ingestion of pig's pancreas, herring's roe, or Liebig's extract increases the excretion of uric acid. The evidence of the origin of the latter from nucleins does not therefore depend on thymus feeding alone. Any disproportion between the excretion of uric acid after flesh diet and the amount of nucleins contained in muscle is probably to be explained by the presence in such diet of alloxuric bases, and especially of hypoxanthine, in sufficient quantity to account for the rise produced. The presence of these bases in flesh probably accounts for the early rise in uric acid after a meal, and will also account for the increase found when pepsin-hydrochloric (nuclein free) extracts of the thymus are taken. Fresh experiments are given showing a rise of uric acid after taking pure nucleins. There is, in fact, no evidence that uric acid can arise in man independently of a substance containing an alloxuric (purine) group.

W. D. H.

**Results of Administration of Indole.** By EYVIN WANG (*Zeit. physiol. Chem.*, 1899, 27, 557—574).—Indole was first recognised as the source of indican in the urine by Jaffé (*Centr. med. Wiss.*, 1872, 1, 2), and urinary indican was shown to be an ethereal sulphate by Baumann (*Zeit. physiol. Chem.*, 1877, 1, 67). Estimation of indican now being possible by the author's method, the present research was undertaken to determine the quantitative relationship of indole given by the mouth, and the indigo of the urine, in dogs. The following results were obtained:—The indole of the alimentary canal is excreted by the urine within 24 hours; 1 gram of indole is sufficient to cause symptoms of poisoning in a medium sized dog; this has been denied by some previous observers (Baumann and Brieger); the quantity of ethereal hydrogen sulphates excreted is smaller than that which would correspond with the amount of indole given; about half of this amount of indole is passed as indigo-forming substance; ethereal hydrogen sulphates other than potassium indoxyl sulphate are formed; the excretion of indigo and of ethereal hydrogen sulphates is not constant

on a fixed diet in the normal condition ; there is also no constant relationship between the indican and the ethereal hydrogen sulphates ; cooking the food makes no difference. W. D. H.

**Pentoses in the Urine.** By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1899, 27, 507—539).—The reactions examined for the detection of pentose in the urine were :—(1) The Tollens reaction with phloroglucinol and hydrochloric acid ; (2) the Tollens reaction with orcinol and hydrochloric acid ; (3) the test with aniline acetate paper ; (4) the occurrence of furfuraldehyde after distillation with hydrochloric acid ; and (5) the preparation of the osazone. Each test is described with full details and the precautions that are necessary. After the use of certain drugs such as menthol and chloral, these tests, especially the first, may be positive without the presence of pentose ; glycuronic acid also may be a source of error. In the presence of dextrose, pentose can still be detected, after the removal of the sugar by fermentation. Three cases of pentosuria are described. The origin of pentose in the body is discussed, and the view that it originates from the nucleoproteids in the pancreas is dismissed. It is regarded as probable that it originates from hexoses. W. D. H.

**Reducing Power of Urine.** By HENRI HÉLIER (*Compt. rend.*, 1899, 129, 58—60).—The author determines the reducing power of urine by mixing 10 c.c. of the liquid with 10 c.c. of concentrated sulphuric acid and adding a solution of potassium permanganate (6.36 grams per litre) until a permanent rose tint is produced. An estimation of the urea is also made in order that the reducing power may be expressed with reference to urine of normal concentration containing 2 per cent. of urea. If  $n$  is the number of c.c. of potassium permanganate solution used and  $m$  the number of grams of urea per litre, then the reducing power  $P = 20n/m$ . Normally,  $P$  ranges from 12.5 to 15, but with pathological urine higher or lower values are found, according to the nature and intensity of the disease. N. L.

**Toxicity of Normal Urine.** By WILMOT P. HERRINGHAM (*J. Pathol. and Bacteriol.*, 1899, 6, 158—179).—The experiments recorded were made on rabbits. Normal human urine is undoubtedly fatal when injected intravenously into these animals. The fatal dose varies very considerably, and is not the fixed quantity upon which Bouchard deduced his 'mathematical' theories on the subject. These theories are subjected to criticism, and when tested by experiment invariably fall to the ground. The difference between morning and evening urine, upon which Bouchard established his well-known theory of sleep and waking, does not exist. Bouchard apparently never made any chemical examination of urine, or at least never published any results. The symptoms that follow injection of the urine are contraction of the pupils, drowsiness, twitchings and convulsions, failure of respiration and heart. The analyses published show that the toxicity and amount of potassium salts vary together. This supports the view, which has already been advanced by numerous investigators, that the toxic agents are the potassium salts ; they will account for all the symptoms except the contraction of the pupils. W. D. H.

**Proteids of Muscle.** By GEORGE N. STEWART and TORALD SOLLMAN (*J. Physiol.*, 1899, 24, 427—459).—The method of fractional heat coagulation can be usefully employed in the separation and quantitative investigation of the muscle proteids. The two principal proteids of muscle are paramyosinogen, a typical globulin coagulating from 45—50°, and an atypical globulin, myosinogen coagulating at about 56 to 63°. Halliburton's myoglobulin is regarded as part of the myosinogen. Von Fürth's soluble myo-fibrin is regarded as part of the paramyosinogen. Both proteids pass readily, either in the muscle itself or in saline extracts, into an insoluble modification, myosin; myosinogen first passing readily into a modification similar to or identical with paramyosinogen. As a rule, paramyosinogen is more abundant in saline (5 per cent. magnesium sulphate) extracts than myosinogen; extracts of muscle made with water contain more myosinogen. No marked quantitative differences in the relative amount of the two proteids could be established in the muscles of different animals, in different muscles of the same animal, or in *rigor mortis*. The method of estimation is not capable of detecting minute differences.

The coagulation of the proteids is accompanied with increase of acidity; this confirms what Halliburton originally stated, and von Fürth denied.

Certain facts indicate that *rigor mortis* is associated with the precipitation of paramyosinogen and myosinogen; still the properties of the proteids in extracts do not afford a complete explanation of the production and resolution of rigor. W. D. H.

**Effect of Removal of the Proteid on the Molecular Concentration and Electrical Conductivity of Muscle Extracts.** By GEORGE N. STEWART (*J. Physiol.*, 1899, 24, 460—463).—The results given show that the conductivity is increased after removal of the proteids; the globulins of muscle extracts (which probably would hold salt more firmly or in greater amount than albumins) depress the conductivity in a greater degree than the proteids of serum or hæmoglobin. No constant difference is as yet made out between the various proteids of muscle extracts. W. D. H.

**Nature of the Action of Antitoxins.** By LOUIS COBBETT (*J. Pathol. and Bacteriol.*, 1899, 6, 193—219).—The experiments recorded were performed with the toxin and antitoxin of diphtheria. They follow very much on the lines of those previously published (this vol., ii, 234) by Martin and Cherry, and the results obtained confirm their view, namely, that the interaction of toxin and antitoxin is a chemical one; neutralisation takes place *in vitro*, provided time is allowed, and the intervention of the living cells of the body is not necessary, as Buchner maintains. W. D. H.

**Presence in the Animal Organism of an Enzyme Capable of Reducing Nitrates.** By E. ABELOUS and ERNEST GÉRARD (*Compt. rend.*, 1899, 129, 56—58).—The filtered aqueous extracts of the liver, kidney, suprarenal capsules, lungs, testes, intestines, ovary and sub-maxillary gland, pancreas, spleen, striated muscle, and brain of the

horse possess the property of reducing alkali nitrates to nitrites, the activity of the various organs decreasing in the order indicated. The reduction is in all probability due to the action of an enzyme, since it does not occur if the extracts have been previously heated at 100°, but is not affected by the presence of antiseptics. The activity of the enzyme varies with the temperature, being very feeble at 0°, attaining a maximum between 20° and 40°, and ceasing altogether at 72°.

N. L.

**Presence of a Soluble Reducing Enzyme in the Animal Organism.** By E. ABELOUS and ERNEST GÉRARD (*Compt. rend.*, 1899, 129, 164—166).—An aqueous or glycerol extract of the kidney of the horse contains an enzyme which is capable of reducing nitrates to nitrites; if the extract is boiled, the ferment is destroyed, and the liquid no longer reduces nitrates. Antiseptics like chloroform, thymol, essence of cinnamon, and sodium fluoride do not destroy the reducing power of the extract, but mercuric chloride (1 in 2000) does. The amount of nitrite formed attains a maximum at a temperature of 40—45°, above this it gradually decreases and becomes *nil* at 71—72°. A mixture of 100 c.c. of the extract, 8 grams of potassium nitrate, and 1 c.c. of chloroform was placed in each of three flasks, the air in two of which was displaced by hydrogen and carbonic anhydride respectively. After standing for 24 hours at 42°, the flask, the air in which had been displaced by hydrogen, contained the greatest amount of nitrite, and the flask with the carbonic anhydride by far the least. The addition of sodium carbonate to the extract favours the formation of nitrite. The extract is inactive after filtration through unglazed porcelain.

The enzyme reduces, not only potassium nitrate, but also ammonium nitrate, it decolorises methylene-blue and seems to reduce butyric acid to butyraldehyde.

H. R. LE S.

**Physiological Action of the Alkaloids derived from Anhalonium Lewinii.** By WALTER E. DIXON (*J. Physiol.*, 1899, 25, 69—86).—*Anhalonium Lewinii* is a small cactus, locally known as “mezcal.” A drink prepared from it has remarkable physiological properties, and is used by certain tribes of Mexican Indians in their religious ceremonies. E. White has confirmed Heffter’s results (*Abstr.*, 1896, i, 267) with reference to the existence of the four alkaloids. Mezcaline, anhalonidine, anhalonine, and lophophorine are all crystalline except the last. The physiological action of each is practically the same. Experiments were made on dogs, cats, and men.

There is no action on the skin, an increased flow of saliva, occasionally vomiting, constipation (in man with small doses), and diarrhoea, with blood-stained stools (in animals with large doses). There is no effect on the blood; there is slowing of the heart and fall of blood-pressure; the effect on the heart is not neutralised by atropine; the vagus is paralysed, the return to normal blood pressure is usually quite sudden. There is no effect on the muscles. Respiration is affected only in toxic doses; it becomes quicker and shallower, and death occurs from failure of the respiratory centre. In animals, there

is first increased reflex activity, then paralysis, which is central in origin. In man, there is a preliminary stage of excitement, followed by one of intoxication, which is very much like that caused by alcohol. There are also a number of interesting subjective sensations: a feeling of 'dual existence,' an increased sensitiveness to odours and to music; but the visual sensations are the most marked; there is a kaleidoscopic display of colours; these can be seen with either eye, and must be of central origin. The colouring of external objects is intensified. The urine contains the drugs, and there is some diuresis. Lophophorine is the most powerful of the alkaloids, but mezcaline is most effective in producing colour visions.

W. D. H.

**Mineral Composition of the New-born Child, and Bunge's Law.** By LOUIS HUGOUNENQ (*Compt. rend.*, 1899, 128, 1419—1421. Compare this vol., ii, 503).—Bunge's law, which states that the epithelial cells of the mammary glands secrete, from the mineral salts of the plasma, the exact amounts of inorganic substances necessary for the development of the offspring, holds in the case of the cat, dog, and rabbit. Analyses of the mineral skeleton of the new-born child and of the ash of human milk, however, show that these differ widely in composition, and hence the law is not applicable to the human species. It is probable that the law holds only for those mammals whose osseous tissues are largely developed during the period of lactation; this is not the case in man, and hence the mother's milk is a less important factor in the development of the human offspring than in that of other mammals.

G. T. M.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Amount of Ash and Cellulose Present in Posidonia Caulini.**  
By FELIX CHANCEL (*Bull. Soc. Chim.*, 1899, [iii], 21, 740—742).—The seaweed, *Posidonia caulini*, after being washed with water, contains 10.9 per cent. of ash, calculated on the dry sample, consisting principally of salts of calcium and magnesium; the cellulose, estimated by digesting the dry plant alterately with bromine water and boiling dilute caustic soda, amounts to 39.5 per cent. Since the amount of cellulose remaining after boiling the seaweed with 50 per cent. aqueous caustic potash for  $2\frac{1}{2}$  hours under a pressure of 15 lbs. per square inch was 15.3 per cent., and wheat-straw under the same conditions yields 17.9 per cent., it appears probable that the weed, which is very plentiful on the southern coasts of France, can be utilised for paper-making.

W. A. D.

**Amount of Pentosans in Vegetable and other Substances.**  
By A. MENOZZI (*Ricerche Lab. chim. agrar. R. Scuola Sup. Agric. Milan*, 1898, 247—249).—The following percentage amounts of pentosans were found in the dry matter of the different substances:—Mulberry

leaves, 5.00 (average of five analyses); excrement of silkworms, 9.48; compressed yeast, 2.18; edible fungi (*Boletus edulis*), 1.93; *Penicillium glaucum*, none. Mulberry leaves and the excrement of silkworms contained 11.16 and 18.07 per cent. of cellulose respectively.

N. H. J. M.

**Oxidising Enzyme from Hellebore.** By PH. VADAM (*J. Pharm.*, 1899, [vi], 9, 515—516).—The stem and fresh leaves of this plant contain an oxydase similar to those studied by Bourquelot and Bertrand, Lépineis, and others. Its ash contains iron, but the presence of manganese is not proved.

H. R. LE S.

**Secretion of Enzymes.** By DIENERT (*Compt. rend.*, 1899, 129, 63—64. Compare this vol., ii, 442).—If a yeast which ferments lactose is grown in different portions of a nitrogenous, nutritive medium containing (a) glucose, (b) galactose, and (c) lactose, and the yeasts subsequently separated, dried, and extracted with water, three solutions containing lactase are obtained, the relative activity of which, in hydrolysing lactose, are represented by the numbers 1, 5, and 6 respectively. The most active solution, however, hydrolyses not more than 6 per cent. of lactose. It thus appears that the acclimatisation of a lactose yeast to galactose is accompanied by an increased secretion of lactase. Similarly, the acclimatisation of bottom yeasts is found to be associated with the production of melibiase.

N. L.

**Decomposition of Glucosides by the Action of Moulds.** By KONSTANTIN A. PURIEWITSCH (*Chem. Centr.*, 1899, i, 702—703; from *Ber. Deut. bot. Ges.*, 16, 368—377).—*Aspergillus niger* decomposes salicin into glucose and saligenin, the former being absorbed by the mycelium, and when solutions of helicin, arbutin, coniferin, æsculin, phloridzin, or hesperidin are covered with the mycelium, these glucosides undergo the same decompositions as emulsin effects. The salicylaldehyde formed by the decomposition of helicin kills the mycelium. *Aspergillus glaucus* and *Penicillium glaucum* behave like *A. niger*, but whilst emulsin or the extract from any of these moulds decomposes amygdalin into glucose, benzaldehyde, and hydrocyanic acid, neither benzaldehyde nor hydrocyanic acid is formed by the action of the living mycelium and the amygdalin solution in this case does not reduce Fehling's solution. The amygdalin is assimilated by the mycelium, with formation of ammonia.

In all cases, the glucosides are decomposed into glucose, which is assimilated by the mould and benzene derivatives which are either assimilated or left in solution. This action is effected by means of emulsin, which diffuses from the mycelium. Apparently an enzyme which inverts the sugar is also present. The benzene derivative is only attacked when all the sugar has been used, and similarly in culture solutions containing glucosides and carbohydrates, the former are hydrolysed only when a certain amount of the latter has been appropriated by the mould.

E. W. W.

**Influence of Mineral Constituents of Water on the Composition of Worts and Yeast Ash.** By FRANCIS E. LOTT (*Bied. Centr.*, 1899, 28, 503—504; from *D. Bierbrauer*, 1898, *Beibl.* No 12).—Water contain-



ing calcium sulphate extracts less phosphates and resin, but as much nitrogen as soft water; the fermentability is diminished and the beer produced has a better taste and a lighter colour. Magnesium sulphate diminishes the amount of extract, but not the percentage of phosphates and nitrogen in the extract; when large amounts are present, the beer has a somewhat rough, hard taste. Sodium chloride causes a separation of phosphates and increases the amount of maltose. Calcium chloride increases the nitrogen in the worts, and diminishes the total maltose and the production of yeast. Nitrates cause diminished amounts of extract, impede fermentation, and readily produce beer of a darker colour. Sodium, potassium, and magnesium carbonates check the diastatic power, increase the amounts of proteids, dissolve the hop-resin, and so produce dark-coloured beer with a rough taste. Hydrogen calcium carbonate diminishes the yield of extract, separates phosphates, and dissolves the resin.

The mineral matters in water influence the composition of yeast, and if the effect is at first harmless, injury may be caused as time goes on; on the other hand, the yeast may become acclimatised and eventually be less affected by the mineral matter. Yeast from worts in soft water was found to contain most of the phosphoric acid (93.9 per cent. of the ash) as potassium salt, whilst the ash of Burton yeast contained considerable amounts of magnesium and calcium phosphates (21.0 and 13.6 per cent.) as well as the potassium salt (63.1 per cent.).

N. H. J. M.

**Experiments with Nitragin.** By HJALMAR VON FEILITZEN (*Mitt. Ver. Förd. Moorkultur*, 1898, 16, 323—324).—Nitragin experiments made in 1896 with grey peas growing on new peat-land showed an increase of about 55 per cent. of straw and 116 per cent. of corn under the influence of inoculation. More recent experiments are described in which grey peas and bastard clover were grown on three plots of 2 acres each, the nitragin being applied to the seed and to the soil respectively. As before, the soil was uncultivated peat-land. The following amounts of produce (in kilos.) were obtained:

	Not inoculated.	Seed inoculated.	Not inoculated.	Soil inoculated.
Grey peas (dried)...	270	1220	100	1340
Clover (green) .....	60	2130	0	1020

N. H. J. M.

**Influence of Ether on Germination.** By C. O. TOWNSEND (*Expt. Stat. Record.*, 1899, 10, 1048; from *Proc. Amer. Assoc.*, 1898, 48, 409—410).—Seeds were soaked in pure water for 24 hours and then transferred to air-tight chambers containing respectively 1, 2.5, 5, and 10 c.c. of ether in 100 c.c. of water. One c.c. of ether slightly expedited germination, but somewhat retarded the subsequent growth. Ten c.c. of ether prevented germination, and in 2 weeks seemed to kill the seeds; when, however, the seeds were removed after 7—10 days, they germinated readily. Similar results were obtained with spores on gelatin plates.

N. H. J. M.

**Behaviour of Calcium Oxalate during the Growth of Vegetable Organs.** By GREGOR KRAUS (*Bied. Centr.*, 1899, 28, 458—459; from *Flora*, 1897, 83, 54—73, and *Bot. Centr.*, 1897, 69, 384).—On growing roots of *Rumex obtusifolius* in pure quartz sand, with and without addition of chalk, it was found that, whilst in presence of chalk there was either no change or else a gain of calcium oxalate in the plants, there was a not inconsiderable loss of oxalate in the plants grown without lime; in some cases, the loss of oxalate diminished to the same extent as the other reserve substances. The oxalate had evidently been utilised to supply the lime necessary for the development of the growth above ground, and it is concluded that this occurs under normal conditions when lime becomes necessary.

In the case of the oxalate in the rind of bushes and trees, it was found that the amount diminished during the formation of buds.

The fact that, in *Cactaceæ*, the amount of oxalate is greatest in the older parts would seem to indicate that it is not used up, but inasmuch as the crystals are mostly in the living parenchyma, it seems possible that the oxalate might be available if required.

A number of experiments made with a variety of vegetable acids showed that the acids present in the cell-sap have the power of dissolving calcium oxalate.

N. H. J. M.

**Formation of Alcohol and Carbonic Anhydride, and Absorption of Oxygen in Plant Tissues.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 128, 1366—1370. Compare *Abstr.*, 1895, ii, 124).—In order to demonstrate conclusively the existence of alcohol in the organs of the living plant, it is absolutely necessary to operate on tissues recently removed with as little mutilation as possible, otherwise appreciable quantities of this substance may be produced by subsequent fermentative changes.

Freshly-cut blades of wheat were introduced into a tared flask and heated to 94° after displacing the air by a current of hydrogen. The carbonic anhydride and alcohol were driven off, and the former estimated by potash absorption. The experiment was repeated with hazel leaves, and a large quantity of material was employed in order to ascertain the nature of the alcohol; in this case, the distillation was conducted in a current of steam, and from 10 kilos. of leaves, about 10 grams of alcohol were obtained, consisting chiefly of the ethylic derivative, together with appreciable quantities of its higher homologues, and a trace of some camphor-like substance; methylic alcohol was not detected.

These results indicate that the tissues of wheat and hazel grown under normal conditions contain small quantities of alcohol, this substance being produced by reactions similar to those which give rise to methylic alcohol in certain other plants. No simple relationship could be traced between the amounts of alcohol and carbonic anhydride; the evolution of gas continues for several hours, and is due to changes which do not involve the formation of alcohol, and the quantity increases when air is admitted during distillation. It follows from this that the variation in the ratio between the carbonic anhydride pro-

duced and oxygen absorbed ("respiratory coefficient") cannot depend on the formation of any one compound such as ethylic alcohol.

G. T. M.

**Production of Alpine Characters in Plants by Extreme Variations of Temperature.** By GASTON BONNIER (*Compt. rend.*, 1898, 127, 307—312).—Experiments on the influence of temperature on growth in the case of plants (clover, wood sage, groundsel, vetch, oat, and barley) capable of growing either at high or low altitudes. The plants were cultivated (1) in enclosures cooled to 4—9°; (2) under the normal summer conditions prevailing at Fontainebleau, the temperature ranging from 15—30°, and occasionally from 10—35°; (3) under conditions alternating between those of series 1 at night and those of series 2 in the daytime, the variations of temperature (4—35°) being comparable with those of Alpine regions; (4) at a uniform temperature of 16°. After an interval of two months (June 3rd to August 1st), the plants of series 3 were found to differ greatly from the others, being more stunted with smaller leaves, and more rapid flowering than even those grown at 4—9°. Hygrometric conditions are shown not to influence growth to any marked degree, and hence variation in temperature is the most important factor in the dwarfing of the alpine flora.

G. T. M.

**[Respiration] of Plants Rendered Alpine Artificially.** By GASTON BONNIER (*Compt. rend.*, 1899, 128, 1143—1146).—The experimental conditions recorded in the preceding abstract were maintained until all the specimens of *Teucrium scorodonia* under investigation had blossomed and fructified (Sept. 16th). The differences presented by the plants are discussed, the most striking changes being found in the leaves. The assimilative power per unit of surface of the leaf showed a great increase in the specimen grown under alpine conditions, and a study of the gaseous exchange between the leaves and the atmosphere indicated that the following amounts of oxygen per sq. cm. of leaf area were evolved during half an hour by plants grown under the conditions 1, 2, and 3, recorded in the preceding abstract.

Series.	1	2	3 (Alpine conditions).
Wood sage ( <i>Teucrium scorodonia</i> )...0.200		0.265	0.271
Clover ( <i>Trifolium repens</i> ) .....0.061		0.05	0.067

G. T. M.

**Modification of Plant Respiration resulting from Variations of Temperature.** By WLADIMIR PALLADIN (*Compt. rend.*, 1899, 128, 1410—1411).—Etiolated stems of *Vicia faba* were weighed out in three portions; the first was kept at a medium temperature (17—20°), the second cooled to 7—12°, and the third heated to 36—37°; after several days, the three were brought to the same temperature, namely, 18—22°, and the amount of carbonic anhydride evolved from 100 grams was determined in each case. The stems which had been cooled evolved 40 per cent., and those which had been

heated 53 per cent. more carbonic anhydride than those which had remained at the medium temperature. These experiments support the conclusions arrived at by Bonnier (preceding abstracts) with respect to the increase in the assimilating power of the leaves of plants grown under alpine conditions.

G. T. M.

**Improvement in the Chemical Composition of the Maize Kernel.** By CYRIL GEORGE HOPKINS (*Univ. Illinois Agric. Expt. Stat. Bul.*, 55, 1899, 205—240).—Whilst the composition of an ear of maize is nearly uniform throughout, different ears of the same variety often vary considerably in composition. It was therefore thought possible that, by selecting grain of known composition, crops might be obtained with high percentage of proteids, carbohydrates, or fat as desired. The results of field experiments commenced in 1896 show that this change can be effected. Selected seed containing a high percentage of proteids produced a crop containing 11·10 per cent. of proteid, whilst seed containing less proteid produced a crop containing 10·55 per cent. Greater differences were subsequently obtained.

In a similar manner, crops were obtained containing 5·15 and 3·99 per cent. of fat respectively. In six experiments, differences of 0·67 to 1·45 per cent. of fat were produced.

The percentage of carbohydrates varying inversely with the combined percentages of proteid and fat, carbohydrates are increased whenever the combined percentage of proteid and fat is decreased.

The amount of proteid in the seed varies chiefly with the proportion of glutinous layer in the kernel, whilst the amount of fat varies uniformly with the proportion of germ. It is thus both possible and practicable to select seed by mechanical examination and without chemical analysis.

N. H. J. M.

**Cultivation of Potatoes and Mangolds at Grignon.** By PIERRE PAUL DEHÉRAIN (*Ann. Agron.*, 1899, 25, 336—350).—Potatoes:—Different varieties of potatoes were manured with 30,000 kilos. per hectare of farmyard manure in addition to the previous crop of vetches which had been ploughed in. There were two plots for each variety of potatoes, one of which had produced a large, the other a smaller, yield of vetches. The average increase of potatoes (tubers), taking all varieties, due to the green manure, was 1·07 ton to each ton of vetches; as the vetches contain about 1 per cent. of nitrogen to 0·3 per cent. in potatoes, the green manure was by no means exhausted.

After discussing the amounts of produce and starch furnished by the different varieties grown under equal conditions, attention is drawn to the great importance of obtaining a change of seed.

**Mangolds:**—Experiments were made in which two varieties of mangolds, very similar in composition, were grown after vetches ploughed in. In addition to the green manure, all the plots except one had farmyard manure (30,000 kilos. per hectare); four plots received in addition sodium nitrate (200 kilos.), three were inoculated with nitrifying soil and four received no further treatment. The plot which had only green manure gave a very fair yield of roots (31,000 kilos). The application of nitrifying soil gave rise, on one plot, to greatly increased production of roots, the yield (59,300 kilos.) being higher than that of

the plot which had nitrate ; on another plot, however, nitrifying soil was without effect.

The amount of nitrogen removed by the roots (the leaves were returned) was about 170 kilos. per hectare, whilst the amount applied to the soil was 322 kilos. (in the form of dung, green manure, and nitrate), leaving 150 kilos. in the soil as organic nitrogen. The average amount introduced on the plots as green manure was 159 kilos. per hectare.

N. H. J. M.

[Analyses of Rothamsted Soils.] By ARTHUR GOSS and HARRY SNYDER (*U.S. Dept. Agric. Div. Chem., Bul. 51, 1898, 73-79*).—Partial analyses were made by the U.S. Department of Agriculture, and at several Agricultural Experiment Stations, of samples of surface soil (9 inches deep) from the following plots : Broadbalk Field (wheat), plots 3 (unmanured since 1843), 10 A (ammonium salts ; N=86 lb.), 11 (ammonium salts and superphosphate), and 13 (ammonium salts, superphosphate, and potash). Hoosfield (barley), plots 1 A (ammonium salts ; N=43 lb.), 2 A (ammonium salts and superphosphate), 3 A (ammonium salts and sodium, potassium, and magnesium sulphates), and 4 A (ammonium salts and complete minerals). The results are given as percentages in dry soil.

The soluble organic matter and nitrogen were determined by extracting with 3 per cent. ammonia and 3 per cent. sodium hydroxide respectively. Owing to the difficulties of the method, the results varied considerably ; the highest and lowest are given here.

	Broadbalk Plot 3.			Hoosfield Plot 2 A.		
	Total N.	Humus.	N in humus.	Total N.	Humus.	N in humus.
Highest .....	0·12	3·29	4·92	0·12	2·93	3·14
Lowest .....	0·09	1·47	1·00	0·10	1·82	1·10
Mean .....	0·102	2·16	2·93	0·110	2·33	2·41

The total phosphoric acid was determined by the Goss method and by digestion with nitric acid ; the total potash by the (1) Smith, and (2) hydrofluoric acid methods. Soluble phosphoric acid and potash were also determined.

	P <sub>2</sub> O <sub>5</sub> .		Total.		K <sub>2</sub> O.		
	Total.	Sol. in (Mean).	Smith	H.F.	Soluble in.		
		N/5HCl.			N/5AmCl.	N/5CaCl <sub>2</sub> .	N/5HCl.
Broadbalk Plot 3 ...	0·119	0·0039	1·20	1·38	0·0118	0·0110	0·019
Hoosfield Plot 2 A...	0·172	0·0357	1·29	1·20	0·0188	0·0097	0·016

The following average results, obtained with soils which have had no phosphates for 53 years (Broadbalk 3 and 10 A ; Hoos. 1 A and 3 A), and with soils which received 350 lbs. of surphosphate each year (Broadbalk 11 and 13 ; Hoos. 2 A and 4 A), show that the methods give results in accordance with known facts.

Without phosphates.			With phosphates.		
Total P <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> sol. in N/5HCl.		Total P <sub>2</sub> O <sub>5</sub> .	P <sub>2</sub> O <sub>5</sub> sol. in N/5HCl.	
0·108	0·0035		0·183	0·0398	

N. H. J. M.

**Influence of various Plants on the Amount of Moisture in the Soil.** By MAX MAERCKER (*Bied. Centr.*, 1899, 28, 436—437; from *Landw. Jahrb.*, 1898, 27, 170).—The amount of moisture in soil growing various crops was determined twice a week. At the commencement (May 21), the amounts of moisture were fairly uniform, except in the case of the oat plot, which was rather dryer than the others. During the first few weeks there was comparatively little change in the case of sugar-beet, potatoes, and peas, whilst the oats, and especially the wheat, took up large amounts of water. In July, the sugar beet began to take up more water, and the soil became almost as dry as that under wheat.

After the peas and the wheat were cut, it was found that the former left considerably more moisture in the soil than the latter, whilst sugar beet takes up as much moisture as any crop when the leaves are fully developed.

N. H. J. M.

**Changes in Butter Produced by Feeding with Fat.** By GEORG BAUMERT and FR. FALKE (*Bied. Centr.*, 1899, 28, 452—454; from *Zeits. Unters. Nahrungs u. Genussmittel*, 1898, Heft. 10, 665).—Two cows were fed during successive periods with different oils, in the form of emulsions, in addition to hay and rape-cake meal freed from fat. During the first and last periods, the oil was omitted. The results of analysis of the butter produced under the different conditions showed, not only that the oil in the food essentially altered the nature of the butter, but that the changes varied in accordance with the character of the oil. The determinations made were the Köttstorff, Reichert-Meissl, and the von Hübl iodine numbers.

The results are thus opposed to those of Soxhlet, which indicated that the fat in food does not pass into the milk, but that it replaces the fat already existing in the body, enabling a portion of the body-fat to migrate to the milk (compare *Abstr.*, 1898, ii, 402).

N. H. J. M.

**Assimilability of Organic Nitrogen in Sterilised Media.** By A. LYEBYEDYEV (*Expt. Stat. Record*, 1899, 10, 723; from *Selsk. Khoz. Lyesov.*, 186, 1897, No. 7, 159—169).—Barley was grown in sand manured with urea, hippuric acid, leucine, aspartic acid, and asparagine respectively, calcium carbonate being added to obtain neutrality. The sterilised cultivations produced very little growth, and seed was only produced in the pots manured with asparagine. In the case of similar pots inoculated with soil extract, the following amounts of dry produce (roots, straw, and grain) were obtained: hippuric acid; 1.05; urea, 0.778; leucine, 4.246; asparagine, 2.942; aspartic acid, 0.920 gram.

Calcium nitrate produced far more growth (over 10 grams) than any of the organic substances.

N. H. J. M.

**Sugar as an Agent in Nitrogen Fixation and an Aid to the Growth of Plants.** By JOHN GOLDING (*J. Soc. Chem. Ind.*, 1899, 18, 564—566).—Lucerne, beans, clover, and sainfoin were grown in pure sand, with mineral manure, both with and without addition of cane sugar (5 and 10 grams). The pots, previously sterilised, were

inoculated with water containing a portion of a crushed nodule taken from a corresponding plant. The following amounts of green produce were obtained (grams).

		Stems, &c.	Lucerne. Roots.	Total.		Beans. Entire plants.
Without sugar	...	25.0	16.3	41.3	...	53.5
With sugar	...	38.1	21.6	59.7	...	62.1

The distinct gain in produce under the influence of cane sugar is attributed to increased energy of the nitrogen-fixing bacteria.

N. H. J. M.

**Composition of Starfish.** By GEORGE WILTON FIELD (*Ann. Rep. Agric. Expt. Stat. Rhode Island*, 10, 1898, ii, 150—165).—Analyses of starfish (*Asterias Fobesii*) obtained in Narragansett Bay, were made in order to ascertain its value as manure. The percentage results in (1) the live unrinsed starfish and (2) the dry matter of the rinsed starfish were:

	N.	Crude ash.	K <sub>2</sub> O.	CaO.	P <sub>2</sub> O <sub>5</sub> .
(1)	1.80	20.34	0.23	9.62	0.20
(2)	5.20	58.84	0.66	27.82	0.57

N. H. J. M.

**Action of Bremen Poudrette on Sandy Soil.** By BRUNO TACKE (*Bied. Centr.*, 1899, 28, 437—438; from *Mitt. Ver. Förd. Moorkultur*, 1897, 15, No. 22, 369).—In order to ascertain the relative value of the nitrogen of poudrette as compared with that of sodium nitrate, winter rye and potatoes were grown in a cultivated, sandy soil, and manured with 21.07 kilograms of nitrogen per hectare in the two forms. Kainite and basic slag were also applied, and the soil, which contained a good deal of humus, had been previously marled. In a second experiment, 42.15 kilograms of nitrogen were employed.

Taking the yield of produce obtained under the influence of nitrogen as 100, the yield of rye manured with poudrette was 58 with the smaller, and 56 with the larger quantity of manure. In the case of potatoes, the action of the smaller amount of nitrogen in the form of poudrette was 65, as compared with 100 for the nitrate. The results of the two experiments taken together show that the nitrogen of the poudrette was equivalent to about 60 per cent. of nitrogen in the form of nitrate, a somewhat higher result than that obtained by Maercker (*Mitt. deut. Landw. Ges.*, 1897, Stek. 17, 218).

N. H. J. M.

**How much Basic Slag should be Applied to Meadows?** By PAUL WAGNER (*Bied. Centr.*, 1899, 28, 439—442; from *Deut. landw. Presse*, 1898, 25, Nos. 1 and 2).—The opinion that 4 cwt. of basic slag per hectare is a sufficient application for the greatest amount of produce is based on an error in Wolff's tables, according to which hay contains 0.43 per cent. of phosphoric acid. Hay from good meadows may contain a considerably higher percentage of phosphoric acid.

According to the amount of phosphoric acid present in the soil, a meadow should receive the first year 12, 16, or 20 cwt. of basic slag, the amount being made up to 24 cwt. the second year. In subsequent

years, 5 cwt. of basic slag (containing 16 per cent. of phosphoric acid) may be applied for every cwt. of hay obtained.

In the case of rich soil, containing, for example, 0.15 per cent. of phosphoric acid, a yearly application of 4 cwt. of basic slag would be sufficient for the best crops. N. H. J. M.

**Manurial Experiments with Sugar Beet.** By MAX MAERCKER (*Bied. Centr.*, 1899, 28, 442—443; from *Landw. Jahrb.*, 1898, 27, 32).—The object of the experiments was to ascertain whether a top-dressing of sodium nitrate has an injurious effect on the amount of sugar produced, and whether different varieties of roots are differently affected by the top-dressing.

The different varieties varied less in amount of roots than in leaf production. Generally, but not invariably, there was a relation between the amounts of leaf and of sugar; varieties which produced least leaf contained 2.72 per cent. less sugar than the varieties with the greatest amounts of leaf.

Omission of nitrogenous manure influenced the yield considerably; but the top-dressing of sodium nitrate had, in these experiments, no effect on the sugar production. Probably the particularly favourable season (1896) prevented any injurious action. N. H. J. M.

**Manurial and Variety Experiments with Barley.** By MAX MAERCKER (*Bied. Centr.*, 1899, 28, 443—446; from *Landw. Jahrb.*, 1898, 27, 94).—Although the soil of the field in which the experiments were made contained 0.25 per cent. of potash, the application of kainite increased the yield of grain 192.3 kilograms per hectare; the quality of the grain was also improved, the grain containing 64.3 per cent. of starch instead of 60.0 per cent.

Excess of nitrogenous manure is injurious, especially when there is a deficiency of mineral matter. Guano gave slightly less grain and straw than sodium nitrate, but the grain was of the best quality. In conjunction with guano, potash was without effect.

As regards the composition of barley, the results given for nitrogen in Wolff's tables are too high both for grain and for straw, and the results for potash in grain are somewhat low. Barley-straw was found to contain 1.65 per cent. of soda (Wolff gives 0.16 per cent.), probably owing to the prolonged use of manures rich in soda. N. H. J. M.

**Determination of the Manure Requirements of Soils.** By GEORG LIEBSCHER and EDLER (*Bied. Centr.*, 1899, 28, 448—452; from *J. Landw.*, 1896, 84).—Pot experiments were made with oats, and both the produce and the soil analysed. The soil contained 0.6—0.7 per cent. of nitrogen, and the application of nitrogenous manure always increased the yield of produce, whilst without nitrogenous manure the produce was poor in nitrogen. Exclusive potash manuring diminished the percentage of nitrogen in the produce, and complete mineral manure had a still greater effect. Without nitrogenous manure, that is, with small amounts of produce, the percentage of phosphoric acid in the produce was comparatively high. Potash manuring increased in every case the amount of potash in the produce, whilst with a com-



plete manure the percentage of potash was lowest. It is concluded that, under equal conditions of cultivation, including temperature and moisture, the analysis of the crops will give trustworthy evidence as to the wants of the soil, inasmuch as results are obtained in accordance with the results of manuring experiments. Von Seelhorst, however, thinks that this method would not have the same value in practice, since plants grown in the field often differ a good deal in composition from those obtained in pot cultures. N. H. J. M.

**Employment of Ammoniacal Manures on Calcareous Soils.** By ERCOLE GIUSTINIANI (*Ann. Agron.*, 1899, 25, 325—335).—Experiments were made to ascertain the effect of different amounts of chalk on ammonium salts in sterilised sand, and the influence of temperature and moisture on the loss of nitrogen as ammonia. Purified air was passed through the sand (200 grams) to which dilute ammonium sulphate had been added, and afterwards through titrated sulphuric acid in which the ammonia was subsequently determined. In the first experiment, there were four flasks with sand, (1) without and (2, 3, and 4) with 0.36, 10, and 40 per cent. of chalk respectively, a fifth flask containing chalk alone. The amounts of water and of nitrogen as ammonia were 5.0 and 0.054 per cent., and the temperature was 12—24°. In absence of chalk, there was no loss of ammonia, whilst with the smallest amount of chalk, there was a loss of 22.8 per cent. in 22 days, and the loss increased slightly with increased amounts of chalk. With chalk alone, the loss was greatest (26.7 per cent.). The same flasks were next subjected to a higher temperature (30—42°) for 18 days. The total loss (40 days) was almost the same in each case (94.3—95.7 per cent.).

A similar experiment, in which dry air was employed, showed that although 60 per cent. of the moisture in the sand was lost in 10 days, nearly all the ammonia was lost in presence of chalk, the proportion of chalk having no appreciable effect on the result.

On substituting basic slag (0.1, 1, and 3 per cent.) for chalk, it was found that the largest amount caused the loss of most of the ammonia in 24 hours. N. H. J. M.

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## Analytical Chemistry.

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**Correct Values of Empirically Divided Hydrometer Scales.**  
By PAUL FUCHS (*Zeit. anal. Chem.*, 1899, **38**, 333—341).—The author gives tables showing the true density (at a stated temperature in each case) corresponding with each degree of a number of hydrometers in use for technical purposes. These include the rational Baumé scale, the Beck and Cartier instruments, Fischer's and two other oil-hydrometers, the percentage salinometer, and a special instrument for the percentage of acetic acid in vinegar. As has frequently been pointed out, the instruments in actual use often deviate seriously both from the intended values and from one another. M. J. S.

**Volumetric Estimation of Sulphur in Cast Iron, Steel, &c., by Arsenious Acid.** By J. THILL (*Zeit. anal. Chem.*, 1899, 38, 342—344).—The metal is dissolved in hydrochloric acid and the evolved gases passed through a mixture of 25 c.c. of *N*/10 arsenious acid and 50 c.c. of cold saturated sodium hydrogen carbonate solutions. The absorption apparatus of E. Franke, or that of Wiggert and von Reis, is recommended, because it is necessary to cool the vapours from the evolution flask. The acid must be added to the metal very slowly, and then kept just at the boiling point until all the metal is dissolved; the gases are then driven over into the absorption vessel by carbonic anhydride. The arsenite is then acidified, made up to 500 c.c., filtered, and 100 c.c. titrated with *N*/50 iodine solution after making alkaline with ammonium carbonate. Very good results are obtained.

M. J. S.

**Estimation of Sulphur in Substances Rich in Iron.** By C. MEINEKE (*Zeit. anal. Chem.*, 1899, 38, 351—352).—The author has compared Lunge's process for the analysis of pyrites with that recommended by himself and by Heidenreich (this vol., ii, 517, 518), and obtained absolutely identical results.

M. J. S.

**Electrolytic Method for Estimating Nitrogen in Organic Substances.** By C. C. L. G. BUDDE and C. V. SCHOU (*Zeit. anal. Chem.*, 1899, 38, 344—348).—The substance is mixed with 4 c.c. of fuming and 8 c.c. of ordinary sulphuric acid, as in the Kjeldahl process, and the liquid is electrolysed. Rapid oxidation ensues, and the nitrogen is converted into ammonia. The apparatus used is a globular flask of 50 c.c. capacity, with a pocket holding 10 c.c. projecting downwards from the bottom. The electrodes, consisting of a cylindrical anode of platinum foil, with a stout platinum wire in its axis for the cathode, are passed to the bottom of the pocket, and the connecting wires, which are protected by glass tubes, are connected with an electric supply of 8 volts. Only a feeble current passes at first, but the current soon rises to about 10 ampères, and the liquid becomes hot. Sulphurous anhydride is given off, and sulphur is often deposited in the neck of the flask. In about 3/4 hour the liquid will, as a rule, have become colourless, although a small, black deposit often forms, and the cathode is covered with a black powder. About half of the sulphuric acid will have disappeared. Excess of soda is added and the ammonia distilled as usual. A great advantage of the process is that no reagent other than sulphuric acid is required, as this greatly facilitates the examination for inorganic constituents. The electrolysed solution may be diluted and treated with hydrogen sulphide before distilling off the ammonia. Most of the substances tried gave results agreeing more closely with theory than those obtained with the ordinary Kjeldahl process, but uric acid and ethylic cyanurate gave low numbers, and the method is altogether inapplicable to cyclic compounds containing more than one atom of nitrogen in the ring.

M. J. S.

**Analysis of Nitrites.** By E. ORLOFF (*Chem. Centr.*, 1899, i, 805; from *Techničeski Sbornik*, 1899, i, 29).—0.1 gram of the nitrite dis-

solved in 10 c.c. of a 10 per cent. solution of potassium iodide is carefully introduced into a Lunge's nitrometer. 25 c.c. of a solution of 1 gram of arsenious acid and 5 grams of sodium carbonate in 200 c.c. of water are then added; this must, however, be first neutralised by hydrochloric acid and freed from carbonic anhydride by boiling. Finally, 2—3 c.c. of strong hydrochloric acid are added. The brown liquid soon becomes colourless as the iodine is absorbed by the arsenious acid, and consequently the mercury remains clear. The volume of the nitric oxide is now read off and reduced to weight.

L. DE K.

**Estimation of Carbon and Hydrogen in Organic Substances containing Nitrogen.** By OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1899, 21, 596—605).—The substance is burnt in a current of purified oxygen, the water being absorbed by calcium chloride, and the carbonic anhydride collected in two soda-lime tubes, a small U-tube containing glass wool moistened with sulphuric acid being placed between the two. When the combustion is finished, the oxygen is swept out by a current of purified air.

When dealing with nitrogenous matter, such as amido- or nitro-compounds, it has not been found necessary to use a spiral of metallic copper, except in the case of picric acid, which appears to yield some nitric peroxide. The soda-lime and the sulphuric acid were afterwards repeatedly tested for nitric compounds, but none were found; moreover, the carbon determinations were quite satisfactory.

L. DE K.

**Carbon Combustions in a Platinum Crucible.** By PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1899, 21, 557—558).—The amount of carbon in steel is estimated as follows:—The sample is treated with an acidified solution of copper potassium chloride, and the carbon collected on asbestos, or a little asbestos is added to the liquid, and then collected on a Gooch crucible. When washed and dried, the asbestos is put, carbon side downwards, into a platinum crucible, taking care that all the carbon is kept within a quarter of an inch of the bottom; if a Gooch crucible has been used, it is placed inside the platinum crucible without its cap. The crucible is then nearly filled with asbestos. The essential part of the apparatus is a water-cooled stopper for closing the crucible; it is made of sheet copper and fitted with a band made of pure black rubber. There is no danger of burning or softening the rubber, for it is cooled by the water passing through the stopper, and also by a wet wick wrapped a few times round the upper part of the crucible, the ends of the wick drawing water from a circular trough kept full by the overflow from the stopper.

The carbon is burnt in a current of purified air, the inlet and outlet tubes for which pass through the stopper, and a blast lamp is used as the source of heat. The products of combustion pass through a small tube containing copper oxide and heated by a single Bunsen burner, and then through a tube filled with glass beads moistened with water, to retain chlorine compounds; no advantage was found to arise from the use of silver sulphate. The gas is then dried over calcium chloride,

and the carbonic anhydride is absorbed in a weighed Geissler potash apparatus.

The apparatus may also be used for other purposes, such as the estimation of carbonic anhydride and water in limestone by ignition.

L. DE K.

**Analysis of Silicon.** By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1899, 38, 350—351).—About 10 grams of potash are dissolved in 100 c.c. of water in a large silver basin, and 0.5 gram of the finely-divided silicon is added while gently warming. The substance readily dissolves, leaving the alumina, ferric oxide, and ferro-silicon which are present as impurities. These are collected on a filter and washed until free from alkali. They are then dissolved in hydrochloric acid and the solution evaporated. After filtration from traces of silica, the ferric oxide and alumina are precipitated by ammonia and weighed together. The iron is then estimated by reduction and titration. Silicon is found by difference.

M. J. S.

**Estimation of Potassium as Platinochloride.** By FRIEDRICH BOLM (*Zeit. anal. Chem.*, 1899, 38, 348—350).—The platinochloride is collected on an unweighed filter (which has been previously washed with hot water and alcohol, and not dried), and is washed with 96 per cent. alcohol. After expelling the adhering alcohol in the oven, the precipitate is dissolved in boiling water and the solution evaporated in a glass or porcelain (not platinum) basin. The salt deposits in concentric rings on the wall of the basin, and can be dried to a constant weight in half an hour at 130°. It may then be reduced by Sonstadt's method (*Trans.*, 1895, 67, 984) by dissolving it in the basin in a little hot water, adding mercury, and stirring while keeping hot, until the solution is colourless.

M. J. S.

**Estimation of Potassium and Sodium [in Rocks].** By EDMOND BONJEAN (*Bull. Soc. Chim.*, 1899, [iii], 21, 691—693).—The process recommended differs from those commonly employed, chiefly in the fact that both sodium and potassium are estimated directly. The solution, from which silica, oxide of iron, alumina, and lime have been removed in the usual way, is evaporated to dryness, and the residue, after expulsion of ammonium salts by ignition, dissolved in water, and the magnesium precipitated as ammonium magnesium phosphate. The phosphoric acid in the filtrate is precipitated by 10 per cent. normal lead acetate solution, and the excess of the latter removed by means of hydrogen sulphide. The potassium is finally converted into potassium platinochloride, from which, after collection, the platinum is precipitated by metallic magnesium, whilst the sodium in the filtrate is weighed as sulphate, after removing excess of platinum by treatment with hydrogen sulphide.

N. L.

**Volumetric Estimation of Zinc.** By POUGET (*Compt. rend.*, 1899, 129, 45—47).—The process described is based on Rollet and Campredon's method for the estimation of sulphur. The acid solution, mixed with sodium acetate, is treated with ammonia until a permanent precipitate is produced, and then excess of hydrogen sulphide solution is added. The liquid is boiled until hydrogen sulphide is completely

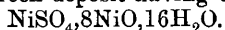
expelled, then mixed with a known volume of standard iodine solution, left for a short time, and the excess of iodine titrated with sodium thiosulphate solution, using starch as indicator. In this process, the troublesome filtration and washing of the precipitated zinc sulphide are avoided; the results are accurate. N. L.

**Kjeldahl's Process for Destroying Organic Matter Applied to the Detection of Metals in Foods, &c.** By A. HALENKE (*Chem. Centr.*, 1899, 1, 551; from *Zeit. Unters. Nahr.-Genussm.*, 2, 128—132).—The following process is recommended for the detection of zinc and other volatile metals, with the exception of mercury, in articles of food: 50 grams of the substance, dried apples, for instance, are boiled with 175 c.c. of sulphuric acid and 1 gram of mercuric oxide for 8 hours in a 750 c.c. Kjeldahl flask; the residue occupying about 10 c.c. is dissolved in 250 c.c. of water, the mercury removed by hydrogen sulphide, and any zinc estimated in the filtrate. For the detection of zinc in flour, 25 grams of the sample are first charred by means of 30 c.c. of sulphuric acid; 3 successive portions of 10 c.c. of acid are then added at intervals of 10 minutes, and after heating for another half-hour, 65 c.c. more acid and 1 gram of mercuric oxide are added and the mixture boiled for five hours. If not sufficiently concentrated, the liquid is transferred to a platinum dish and boiled down to 20 c.c. The residue is then dissolved in water and treated as directed. The test analysis is satisfactory. L. DE K.

**Titration of Iron in Hydrochloric Acid Solution.** By WILLENZ (*Chem. Centr.*, 1899, 1, 638—639; from *Ann. chim. anal. appl.*, 4, 37—41).—The author recommends a process originated by Reinhard, but now almost forgotten (compare, however, *Abstr.*, 1898, ii, 646). 60 grams of tin are dissolved in 250 c.c. of hydrochloric acid of sp. gr. 1.19 and then diluted to 500 c.c.; after filtering, 500 c.c. of acid of sp. gr. 1.12 are added and then 1 litre of water. A solution is also prepared containing 200 grams of crystallised manganous sulphate in a litre of water and mixed with 200 c.c. of sulphuric acid. To the boiling solution of the ferric salt the solution of the tin is gradually added until the yellow colour has completely vanished; large excess should be avoided. The source of heat is now removed and 60 c.c. of the manganese solution, 600 c.c. of cold water and 50 c.c. of a cold-saturated solution of mercuric chloride are added and the iron at once titrated with permanganate. L. DE K.

**Influence of Ammonium Salts on the Precipitation of Nickel by Ammonia.** By ARTHUR MARSHALL (*Analyst*, 1899, 24, 202—205).—Unless a large excess of ammonium salts or free ammonia are present, dilute ammoniacal solutions of nickel are apt to deposit a large quantity of the metal as a basic salt, particularly on warming; the presence of sufficient tartaric acid, however, prevents the precipitation.

In one experiment, about 60 per cent. of the nickel present was precipitated as a light green deposit having the composition



Cobalt and zinc behave in a similar manner.

L. DE K.

**Separations of Metallic Sulphides by Means of Hydrogen Chloride.** By J. BIRD MOYER (*J. Amer. Chem. Soc.*, 1899, 21, 642—645).—The sulphides of arsenic, antimony, or bismuth may be separated from lead sulphide by passing hydrogen chloride over the heated mixture; sulphide of arsenic may also be separated from sulphides of cadmium or silver in a similar manner. The non-volatile sulphides are converted more or less completely into chlorides during the process. J. J. S.

**Analysis of Water.** By GEORGE H. BAILEY and J. H. JOHNSTON (*J. Soc. Chem. Ind.*, 1899, 18, 455—457).—*Use of phenolphthalein as an indicator.*—When determining the acidity in water by titrating with standard alkali, using phenolphthalein as indicator, the results may be vitiated by the presence of ammonium salts. If to a solution of ammonium chloride phenolphthalein and solution of sodium hydroxide are added, a considerable quantity of the latter may be added before the liquid turns red; on diluting, it is decolorised and then consumes another portion of alkali; the process is also considerably influenced by the temperature.

*Collection and examination of samples of water.*—The authors show the necessity of having the bottles completely filled and carefully stoppered; even then the analysis ought not to be delayed. Examples are given where the free ammonia, originally large, had completely disappeared in a fortnight, and the albuminoid ammonia had also much diminished. This is due to oxidation by the oxygen dissolved in the water, as proved by the proportional increase in the nitrites and nitrates.

*Acidity of boiler waters and steam.*—Acid waters act seriously on the boiler, but not until the acidity (calculated as hydrogen chloride) reaches nearly 1 per cent. will there be any danger of acid escaping with the steam and injuring the steam valves. Acid may be liberated in the boiling water by decomposition of certain neutral salts, such as magnesium chloride. L. DE K.

**Use of Hyposulphite for Titration, especially for the Estimation of Oxygen in Water and Sewage Effluents.** By B. WILLIAM GERLAND (*J. Soc. Chem. Ind.*, 1899, 18, 340—342).—The author gives further instructions as to the estimation of dissolved oxygen in waters, the method employed being substantially the same as the one described in a former paper (*J. Soc. Chem. Ind.*, 1896, 15, 16). Ordinary coal gas is still employed to displace the air in the apparatus after being freed from oxygen by passing it through an iron pipe filled with copper filings and heated to redness. As regards the indigo used in the process, it is of importance to use a preparation which, when treated with solution of hyposulphite (hydrosulphite), shall change to a yellow, and not to a brown, colour; such indigo may be prepared as follows: indigo is treated with hydrochloric acid, washed, digested with weak caustic soda or ammonia, washed, dried, and crystallised from boiling nitrobenzene. The crystals are washed with benzene, dried, warmed with hydrochloric acid, roughly washed and digested for some hours with hydrogen peroxide or ammonium persulphate in acid solution. After filtering, the product is first

washed with water, then with weak ammonia, and when dry exhausted with strong alcohol. After drying at  $110^{\circ}$ , it may be regarded as pure indigotin, which is then dissolved with the usual precautions in strong sulphuric acid.

L. DE K.

**Distinctions between Mercuric Cyanide and Oxycyanide.** By VON PIEVERLING (*Chem. Centr.*, 1899, i, 504; from *Pharm. Centr. Halle*, 39, 615—616).—Mercuric cyanide forms well-defined crystals, is more readily soluble in water than the oxycyanide, and is neutral to test-paper, whilst the oxycyanide forms a yellowish, crystalline powder having an alkaline reaction. The oxycyanide is precipitated by ammonia or tannin, and also by disodium hydrogen phosphate or potassium chromate in the presence of ammonia; these precipitates are rapidly reduced by stannous chloride. If a solution of mercuric cyanide (1:20) is mixed with a solution of potassium iodide (1:3), crystals of silvery lustre are gradually formed, which dissolve in ammonia and more water to a colourless liquid. A solution of the oxycyanide (1:20), when similarly treated, turns yellow and becomes turbid and orange-red on adding ammonia. On standing, a reddish-brown precipitate is formed, which is soluble in potassium iodide; this solution also deposits silvery crystals.

L. DE K.

**Distinction between Mercuric Cyanide and Oxycyanide.** By WILLY WOBBE (*Chem. Centr.*, 1899, i, 504—505; from *Pharm. Centr. Halle*, 39, 934—935).—The author criticises von Pieverling's paper (preceding abstract) and states that the tests fail with dilute (1 per cent.) solutions. The following tests are proposed: the oxycyanide forms a micro-crystalline, faint yellowish, and faintly alkaline powder. Its 5 per cent. solution is precipitated by tannin and reduced by stannous chloride, whilst ammonia yields a precipitate soluble in excess. Disodium hydrogen phosphate or potassium chromate gives a precipitate soluble in ammonia. A 5 per cent. solution of potassium iodide, added drop by drop, gives a yellow coloration, turning red on adding ammonia; after a while, a reddish-brown precipitate forms, which is soluble in potassium iodide. Hydrogen sulphide or ammonium sulphide precipitates mercuric sulphide.

L. DE K.

**Mercuric Oxycyanide.** By VON PIEVERLING (*Chem. Centr.*, 1899, i, 505; from *Pharm. Centr. Halle*, 40, 22—23).—The author, in reply to Wobbe (preceding abstract), states that the commercial oxycyanides vary much in composition and rarely agree with the formula  $\text{HgO}, \text{HgCy}_2$ ; this explains the varying surgical value of these preparations. The author agrees that, to make his tests work well, strong solutions should be employed.

A proper article should conform to the following test: 3 c.c. of its 5 per cent. solution should give a deep yellow colour on adding 3 drops of a 50 per cent. solution of potassium iodide.

L. DE K.

**Estimation of Alcohol and Ether in the Presence of Light Petroleum.** By HENRY DROOP RICHMOND (*Analyst*, 1899, 24, 201—202).—*Estimation of alcohol.*—20 c.c. of the mixture are shaken with 25 c.c. of water, saturated with ether, and the volume of the



etheral layer (A) is noted. The aqueous layer is drawn off and the liquid is again shaken with 25 c.c. of etherised water; the volume (B) of the ethereal layer is then again noted. Then  $2A - B$  gives the volume of ether and light petroleum and  $(20 + B - 2A) \times 5$  equals the percentage by volume of alcohol in the original mixture.

*Estimation of light petroleum.*—A mixture is prepared of 20 c.c. of 90 per cent. sulphuric acid and 20 c.c. of glacial acetic acid. When cold, 10 c.c. of the sample is introduced into a burette and the acid is gradually added, the mixture being well shaken after each addition. The ether and alcohol are completely dissolved and the volume of light petroleum is then read off. Two satisfactory test-analyses are given.

L. DE K.

**Chemistry and Analysis of Wine.** By MAXIMILIAN RIPPER (*Chem. Centr.*, 1899, i, 548—549; from *Zeit. Landw. Vers.-Wes. Öst.*, 2, 12—23).—The author calls attention to the importance of the ethereal salts in wine. Claret, for instance, is medicinally preferable to white wines, notwithstanding that it contains more tannin, on account of its larger percentage of volatile ethereal salts. The author divides the ethereal salts into two classes, volatile and non-volatile. Those which are volatile are divided into compounds which distil unaltered and others which suffer decomposition; a quantitative separation of these two groups is as yet impossible. The chief constituent of the first group is ethylic acetate, whilst small quantities of ethylic butyrate and ethylic succinate are also present; in practice, these may be expressed as acetate. The author contradicts the statement that the volatile ethereal salts of wine are only saponified by hot alkalis, as it was found that, with a reasonable excess of potassium hydroxide dissolved in proof-spirit, saponification was complete within an hour. Allowance must, of course, be made for the volatile acid accompanying the ethers when estimating their amount by the saponification process.

The detection and separation of the non-volatile ethereal salts in wine is beset with difficulties, and the author has only isolated ethylic tartrate and glyceric tartrate.

L. DE K.

**Analysis of Wines.** By MAX BARTH (*Chem. Centr.*, 1899, i, 550; from *Zeit. Unters. Nahr.-Genussm.*, 2, 106—118).—The product obtained by fermenting pressed out grapes often mixed with stalks consists of an inferior wine with a large extract in which tannin predominates. To identify such a wine or to detect its presence in other wines, a new colorimetric method for the estimation of tannin has been devised.

A standard solution is prepared containing in 100 c.c. 0.2 gram of acetic acid, 6 grams of alcohol and 0.05 gram of pure tannin. Of this, 10 c.c. is mixed in a Desaga's tannin tube with 1 c.c. of a 20 per cent. solution of sodium acetate and 5 drops of a 10 per cent. solution of ferric chloride. A black liquid is obtained, quite opaque on the top and only just transparent when viewed through the elongated bottom part of the tube. More dilute solutions for comparison cannot be prepared from this, as oak bark tannin gives on dilution quite different tones to cœnotannin; the solution actually used

for comparison is therefore prepared as follows: An alcoholic extract is made of fresh, undried grape stones, which is then diluted with water containing 0.2 per cent. of acetic acid until the coloration obtained on adding ferric chloride is the same as that given by the standard solution. This solution can be diluted to any desired extent for purposes of comparison.

The sample to be tested must be quite clear and its acidity is rendered exactly 0.2 per cent. by volume, either by partially neutralising or else by carefully adding acetic acid. If it should contain more tannin than the standard solution, it must be suitably diluted with water containing 0.2 per cent. of acetic acid. The ferric chloride should be put into the two tubes at as nearly as possible the same moment.

L. DE K.

**A New Principle for the Testing of Sugared ("Gallisierter") Wines.** By MÖSLINGER (*Chem. Centr.*, 1899, 1, 549—550; from *Zeit. Unters. Nahr.-Genussm.*, 2, 93—106).—The author states that sugared wines invariably show a less amount of residual acidity than true wines. This residual acidity is found by subtracting from the total acidity the acidity due to the volatile acids calculated as tartaric acid, and also the free and half-combined tartaric acid; the figure obtained is not less than 0.28 per cent. in genuine wines.

As it is possible to defeat this test by adding citric acid, the author has devised a simple method for the detection of that acid. 50 c.c. of the sample are evaporated to a thin syrup and then mixed slowly with 70—80 c.c. of 95 per cent. alcohol. (Free tartaric acid must first be removed by adding a calculated quantity of potassium hydroxide and so converting it into potassium hydrogen tartrate.) The filtrate is freed from alcohol by evaporating to 10 c.c.; 5 c.c. of this is then mixed with 0.5 c.c. of acetic acid and a strong solution of lead acetate is added; if citric acid is present, a precipitate is obtained which disappears on heating. The hot liquid, if turbid, is filtered, and any citrate precipitate will then reappear on cooling.

L. DE K.

**New Method for the Analysis of Commercial Phenols.** By SAMUEL B. SCHRYVER (*J. Soc. Chem. Ind.*, 1899, 18, 553—556).—The process is based on the fact that phenol and its homologues (1 mol.), when acting on sodamide, liberate ammonia (1 mol.). About 1 gram of finely-powdered sodamide is washed a few times by decantation with small quantities of benzene, and then introduced into a 200 c.c. distilling flask fitted with a separating funnel and with an inverted condenser in connection with an apparatus for absorbing ammonia, and this in turn with an aspirator. About 60 c.c. of benzene are introduced into the flask, and this is boiled on the water-bath for 10 minutes, a slow current of dry air, free from carbonic anhydride, being drawn through in order to free the apparatus and contents from ammonia. 20 c.c. of *N* sulphuric acid are then placed in the absorption apparatus, and the solution of the phenol in pure benzene (freed from any moisture by prolonged contact with fused sodium acetate) then introduced into the distilling flask and the boiling continued; the ammonia evolved is absorbed by the standard

sulphuric acid, the excess of which is then titrated with sodium carbonate, using methyl-orange as indicator.

The method may be successfully employed for the estimation of phenols in essential oils, such as guaiacol in wood tar, thymol in oil of thyme, and eugenol in oil of cloves. If the total weight of two phenols is known, their respective amounts may be approximately calculated from the amount of ammonia evolved.

Water in phenols may be estimated by making two experiments, one before, and one after drying; the difference in ammonia represents moisture.

L. DE K.

**Volumetric Estimation of Glucose.** By LÉON GARNIER (*J. Pharm.*, 1899, [vi], 9, 326—330. Compare this vol., ii, 529).—This process is a modification of the Haen-Lehmann method, and is carried out as follows:—50 c.c. of Fehling's solution (10 c.c. = 0.05 gram glucose) are placed in a porcelain dish, diluted with an equal volume of water, and heated to boiling, and to this is added a volume of the glucose solution insufficient for the complete reduction of the Fehling's solution. The liquid is boiled for 2 minutes and poured into a 250 c.c. flask, which is filled to the graduation mark with boiling distilled water. The whole is rapidly cooled, accurately diluted to 250 c.c., and thoroughly mixed, the flask then corked and left for 2—6 hours until the liquid is quite clear.

The excess of Fehling's solution is determined thus:—To 25 c.c. of the clear solution contained in a stoppered flask are added 1 c.c. of dilute sulphuric acid (1 : 3) and 10 c.c. of iodine solution, prepared by dissolving 1 gram of iodine and 1.5 grams of potassium iodide in 200 c.c. of water. The flask is corked and left for ten minutes, a little starch paste is added, and then thiosulphate solution (1 c.c. = 1 c.c. iodine solution) in slight excess; the blue colour is brought back by the careful addition of iodine solution. The strength of the iodine solution is determined by titrating 5 c.c. of the Fehling's solution in the manner just described. From the data so obtained, the volume of Fehling's solution reduced by the glucose is readily calculated.

H. R. LE S.

**Estimation of Methylated Pentoses.** By EMIL VOTOČEK (*Chem. Centr.*, 1899, i, 642; from *Zeit. Zuck.-Ind. Bohm.*, 23, 229—241. Compare *Abstr.*, 1897, i, 405).—The compound, such as rhamnose, is distilled with hydrochloric acid of 12 per cent. strength, the liquid in the distilling flask being constantly replenished with acid, until 400 c.c. have been collected in the receiver; strong hydrochloric acid is then added to make up to 500 c.c., the liquid being now supposed to contain 12 per cent. of hydrogen chloride. Two hundred c.c. of the liquid are mixed with about three times as much pure, powdered phloroglucinol as is actually required, and after some time the precipitate, consisting of methylfurfuraldehyde-phloroglucide, is collected, washed until the red colour has changed to yellow, dried at 110° in a current of hydrogen, and weighed. The compound may contain an admixture of furfuraldehyde-phloroglucide, but the joint amount of methylfurfuraldehyde and furfuraldehyde may be calculated with reasonable accuracy by multiplying the weight obtained by 1.024. To estimate methylfurfuraldehyde and furfuraldehyde in the presence

of each other, Schiff's reaction may be utilised. One hundred c.c. of the distillate are neutralised with soda, acetic acid is added until its amount reaches 5 per cent., and an alcoholic solution of xyloidine is added, which gives a red coloration with the furfuraldehyde. After remaining for half an hour in the dark, the liquid is tested in a Krüss colorimeter, using as the liquid for comparison a 0.01 per cent. solution of furfuraldehyde in 5 per cent. acetic acid mixed with xyloidine solution. If much methylfurfuraldehyde is present, the yellow colour of the methylfurfurylidenexyloidine interferes with the red colour, so that in such a case the test should be made in gas-light. The process is not trustworthy if only relatively small quantities of methylfurfuraldehyde are present, as it is then no longer admissible to estimate this by difference; a direct colorimetric test for this substance has yet to be found.

The presence of methylfurfuraldehyde in the acid distillate of the seeds of beet shows these to contain methylpentoses. L. DE K.

**Influence of Temperature on the Specific Rotation of Sucrose, and a Method of Correcting Readings of Compensating Polariscopes therefor.** By HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1899, 21, 568—596).—The author has made a lengthy investigation as to the influence of temperature on the specific rotatory power of sucrose and has tabulated the results.

It is now proved beyond doubt that the rotatory power of sucrose at 17.5° is 66.547, whilst at 4° it is 66.657, and at 40°, 66.299. It therefore increases when the temperature falls and decreases as the temperature rises, but the mean rate of increase is not the same at every temperature, as it appears to be greater from 15° to 17.5°, from 20° to 25°, and from 30° to 35° than at other points at which the observations were made.

L. DE K.

**Estimation of Pentosans and its Application to Food Analysis.** By OTTO HEHNER and WILLIAM P. SKERTCHLY (*Analyst*, 1899, 24, 178—183).—An important factor in the analysis of such articles as cocoa, pepper, mustard, coffee, &c., is the amount of husk. This may be determined by the well-known acid-alkali method, but the authors have found that much better results are obtained by estimating the amount of pentosans and calculating the husk from these constituents.

Black pepper, for instance, gave about twice as much crude fibre as white pepper, but it yielded three times the amount of pentosans. Pressed cocoa contains 6—7 per cent. of crude fibre, and cocoa-shell powder about 12 per cent., but whilst the former contains only 2 per cent. of pentosans, the shells contain 8—9 per cent. Pure mustard flour contains but little pentosan, whilst mustard husk contains a large quantity. There is also a decided difference in the amount of pentosan yielded by coffee and chicory.

The results are fully explained and tabulated. The analytical process used is the one recommended by Tollens and Krüger (*Abstr.*, 1897, ii, 353) coupled with Counciler's method for the estimation of furfuraldehyde (*Abstr.*, 1895, ii, 144).

L. DE K.

**Estimation of Starch in Sausage Meat.** By HENRICH WELLER (*Zeit. anal. Chem.*, 1899, 38, 375; from *Forsch. Lebensmittel, &c.*, 3, 430; *Zeit. Unters. Nahr.-Genussm.*, 1, 167).—Use is made of the solubility of starch in zinc chloride and the optical activity of the solution. 40 grams of the finely divided material are mixed with 100 c.c. of water, 0.3 gram of zinc chloride, and 0.5 gram of hydrochloric acid of sp. gr. 1.19, and heated for half an hour in boiling water. After cooling, it is made up to 200 c.c. with water, and the turbid liquid strained. Of this, 50 c.c. are mixed with 0.3 gram of zinc chloride and 0.5 gram of hydrochloric acid and heated to boiling; after cooling, it is made up to 100 c.c. with cold saturated mercuric chloride solution, by which means the optically active proteids are precipitated. The clear filtrate is then polarised in a 200 mm. tube. The different starches exhibit different rotations,  $1^\circ$  Ventzke corresponding with 0.37732 gram of potato starch (in 40 grams of substance), 0.40966 gram of wheat starch, or 0.48284 gram of rye starch. The variety of starch must therefore be ascertained by microscopic examination. The method does not serve for sausage meat containing liver, in consequence of the presence of glycogen and other optically active substances.  
M. J. S.

**Detection of Maize Starch in Wheat-Flour.** By KARL BAUMANN (*Chem. Centr.*, 1899, 1, 547; from *Zeit. Unters. Nahr.-Genussm.*, 2, 27—29).—The author finds that chloral rapidly gelatinises both maize and wheat starches, and cannot therefore be successfully used for distinguishing between them. A more suitable reagent is a solution of potassium hydroxide of 1.8 per cent. strength. 0.1 gram of the suspected flour is treated in a test tube with 10 c.c. of the alkali for 2 minutes, and the alkali is then nearly neutralised by adding 4—5 drops of 25 per cent. hydrochloric acid. The wheat starch is completely gelatinised by this treatment, whilst the maize starch remains intact and may be readily recognised microscopically. Rye-flour gelatinises even more quickly than wheat-flour.  
L. DE K.

**Examination of Commercial Flour.** By HENRY KRAEMER (*J. Amer. Chem. Soc.*, 1899, 21, 650—663).—Details are given of micro-chemical methods for the detection of maize in wheaten flour.

**Detection of Formaldehyde by Means of Phloroglucinol.** By LUDWIG VANINO (*Chem. Centr.*, 1899, i, 710; from *Pharm. Centr. Halle*, 40, 101—102).—The author (compare *Abstr.*, 1898, 2, 545) recommends Jorissen's phloroglucinol test for the detection of formaldehyde in milk. 8—10 c.c. of the sample are mixed with 1—2 c.c. of a 0.1 per cent. solution of phloroglucinol and a few drops of aqueous soda. A reddish coloration is noticed even when the milk contains but 4 parts of formaldehyde per million. The reaction is most pronounced with liquids containing 0.5 per cent., but if larger quantities of formaldehyde are present, the test becomes less distinct, and with more than 3 per cent. fails altogether.  
L. DE K.

**Detection of Formaldehyde in Food Stuffs.** By FERDINAND JEAN (*Chem. Centr.*, 1899, 1, 641; from *Ann. chim. anal. appl.*, 4, 41—42).—The substance to be tested is rubbed to a thin paste with water containing about one per cent. of sulphuric acid. When dealing with milk, 100 c.c. of the sample are mixed with 4 drops of sulphuric acid, heated in a 300 c.c. flask to 80° for a few minutes, and, after adding excess of dry powdered sodium sulphate, 50 c.c. are distilled. The distillate is then tested for formaldehyde. It turns red on adding a solution of magenta previously decolorised by sulphurous acid; with aqueous solution of aniline, a milky turbidity is obtained, and with Nessler's reagent a yellowish- afterwards brownish-red, precipitate is formed. Phenylhydrazine hydrochloride gives a white turbidity, and an alkaline solution of sodium nitroprusside a blue colour; these tests distinguish it from acetaldehyde which gives a reddish colour.

To make perfectly sure, the following test should be applied:—The distillate is mixed with 3 drops of sulphuric acid and ten drops of dimethylaniline and heated for 1—2 hours in a sealed tube at 40° with frequent shaking; the contents are then put into a porcelain dish, made alkaline with soda, and boiled to expel the dimethylaniline. A slight excess of acetic acid is added and then a trace of lead dioxide, when an intense blue colour will develop should formaldehyde have been present. By this process any formaldehyde which has entered into combination with proteids is also liberated. L. DE K.

**Estimation of Organic Acids in Urine.** By LEO STEINDLER (*Chem. Centr.*, 1899, i, 643; from *Österr. Chem. Zeit.*, 2, 70).—The sample of urine is first titrated with standard acid, using methyl-orange as indicator; this shows the point when the first traces of organic acid are being liberated. The titration is now repeated, using as indicator a solution of dimethylamidoazobenzene, which will turn red the moment the organic acids are completely liberated; the difference between the two titrations is due to organic acids, which may be conveniently expressed in terms of hydrochloric acid. The author believes that the process involves no serious sources of error.

L. DE K.

**Quantitative Separation of Isovaleric and Acetic Acids.** By ALFRED C. CHAPMAN (*Analyst*, 1899, 24, 114—116).—The mixed acids are carefully neutralised with sodium hydroxide, the water is distilled off under reduced pressure, and the residue dried for a short time at 100°; it is then powdered and boiled with acetone, which must contain exactly 0.5 per cent. of water, when the sodium isovalerate alone dissolves; the liquid is filtered hot, and the residue is washed with hot acetone. After distilling off the solvent, the sodium isovalerate is treated with sulphuric acid to convert it into sodium sulphate, which is then weighed; the undissolved sodium acetate is also converted into sulphate, and from the amounts of sulphate obtained the quantities of the respective acids are calculated.

L. DE K.

**Wine-Vinegar.** By K. FARNSTEINER (*Chem. Centr.*, 1899, i, 710—711; from *Zeit. Unters. Nahr.-Genussm.*, 2, 198—209).—Three samples of wine were mixed with one-fifth of their bulk of wine-vinegar and allowed to undergo acetous fermentation. Of each three analyses were made, one at the beginning of the experiment, one some three weeks later, and another after four months. The results, which have been tabulated, show a large decrease in alcohol and also a loss in solid matter. The amount of total fixed acidity has decreased, but as the tartaric acid remains unchanged, the loss must have been caused by the disappearance of malic acid. A volatile substance having strong reducing properties, although seemingly not an aldehyde, has been detected in four years old wine-vinegars, but not in commercial samples.

L. DE K.

**Detection and Separation of some Unsaturated Fatty Acids.** By K. FARNSTEINER (*Chem. Centr.*, 1899, i, 545—547; from *Zeit. Unters. Nahr.-Genussm.*, 2, 1—27).—*Conversion of oleic acid into elaidic acid by nitrous acid, and separation of elaidic acid from other unsaturated acids.*—Oleic acid may be separated from elaidic acid by treating the mixed lead salts with ether, in which the elaidate is insoluble; or the mixture may be treated with hot benzene, when the elaidate will separate in crystals on cooling. The best way to convert oleic acid into elaidic acid is to act on 1 gram of the acid at 10—20° with 20—25 c.c. of nitric oxide in an apparatus from which the air has been removed; an equal volume of oxygen is then introduced, and the flask is well shaken. The elaidic acid, which, however, contains about 14—18 per cent. of oleic acid, is then obtained as a bluish- or greenish-white substance which may be reduced to powder, and melts at 43°.

*Estimation of oleic acid.*—Dried barium oleate is practically insoluble in benzene; if 5 per cent. of 95 per cent. alcohol is added, it dissolves on boiling, but practically all deposits on cooling. The barium salts may be obtained directly by heating the fats for 15 minutes with a solution of barium hydroxide in a mixture of equal volumes of benzene and methylic alcohol.

A table is given showing the amount of saturated acids, unsaturated acids, and oleic acid in olive oil, ground-nut oil, lard, and cocoa butter.

*Detection and estimation of linoleic acid.*—By brominating liquid fatty acids Hazura has obtained the compounds  $C_{18}H_{32}O_2Br_4$  and  $C_{18}H_{30}O_2Br_6$ . On reduction, the first yields linoleic acid, and the second linolenic acid. A process of estimating the tetrabrominated compound is based on its sparing solubility in light petroleum. When both occur together, they are dissolved in 50 times their weight of benzene, an equal volume of absolute alcohol is added, and the solution is titrated hot with standard alcoholic potash, with phenolphthalein as indicator. On cooling, potassium hexabromolinolenate is deposited, whilst potassium tetrabromolinoleate remains in solution.

L. DE K.

**Estimation of Oxalic Acid in Urine.** By ERNST SALKOWSKI (*Zeit. anal. Chem.*, 1899, 38, 394; from *Centr. med. Wiss.*, 1899, 257).—Advantage is taken of the solubility of oxalic acid and almost

complete insolubility of phosphoric acid in ether. Half a litre of urine is evaporated to one-third, mixed with 20 c.c. of hydrochloric acid of sp. gr. 1.12, and thrice extracted by shaking with 200—250 c.c. of ether containing 5—10 per cent. of alcohol. The ethereal extract is filtered through a dry filter, distilled, and after addition of water concentrated to about 20 c.c., the solution made feebly alkaline with ammonia, mixed with 1—2 c.c. of calcium chloride, and acidified with acetic acid. The precipitate of calcium oxalate is weighed in the usual manner. With a mixed diet, human urine contains 0.128 gram of oxalic acid per 100 grams of nitrogen. M. J. S.

**Solubility of Calcium Tartrate.** By HENRIK ENELL (*Zeit. anal. Chem.*, 1899, 38, 368—369; from *Nordisk. farm. tid.* 1896).—At 15°, 1 part of calcium tartrate dissolves in 2630 parts of water, 3850 parts of glacial acetic acid, 296—303 parts of 25 per cent. acetic acid, 2280 to 5242 parts of concentrated potassium hydrogen tartrate solution, or 350—385 parts of 3 per cent. acetic acid saturated with potassium hydrogen tartrate. Potassium hydrogen tartrate containing calcium may be readily purified by washing with dilute acetic acid (compare *Abstr.*, 1897, ii, 608). M. J. S.

**Estimation of Uric Acid.** By E. MALLET (*Zeit. anal. Chem.*, 1899, 38, 396—397; from *Ann. chim. anal. appl.*, 4, 82).—The uric acid is precipitated as copper salt by mixing 100 c.c. of urine with 10 c.c. of a 16 per cent. solution of sodium carbonate and taking 82 c.c. of the filtrate for the precipitation of the copper salt. The latter, after washing until free from alkali, is dissolved in 500 c.c. of water containing 5 c.c. of sulphuric acid, and titrated with *N*/10 permanganate. The number of c.c. of permanganate expresses directly the number of centigrams of uric acid per litre of urine. M. J. S.

**Preparation of Homogentisic Acid and its Detection in Urine.** By KARL H. HUPPERT (*Zeit. anal. Chem.*, 1899, 38, 395—396; from *Deut. Arch. klin. Med.*, 64).—The urine, concentrated to one-sixth, is shaken with  $1\frac{1}{2}$ —2 vols. of ether; the residue from the ethereal extract is dissolved in water, and the boiling solution precipitated by a copious addition of lead acetate, the dark coloured precipitate being immediately removed by filtration. The crystals, which will have deposited from the filtrate by the following day, are collected, washed well with water, and treated with hydrogen sulphide in boiling water. The solution is freed from hydrogen sulphide by heating to 55—60° in a vacuum, and the precipitation with lead acetate, &c., repeated until a white lead salt is obtained. The acid solution obtained from this deposits crystals when concentrated in a vacuum over sulphuric acid. A further quantity may be obtained from the mother liquor of the first crop of crude lead salt by treating with hydrogen sulphide, concentrating the filtrate, triturating with solid lead acetate, and washing the paste on a suction filter, first with a saturated lead acetate solution, and then with water. This precipitate is then purified as before.

On moistening the solid acid with potash solution and allowing access of air, the crystals become surrounded with a dark green border



which persists as long as any of the substance remains undissolved, and passes then into brown. If the crystals are completely immersed in the liquid, the brown coloration is obtained at once. A solution of the crystals in methylic alcohol treated with sodium methoxide exhibits a blue colour in thin layers (compare Abstr., 1897, ii, 576; 1891, 1129; 1892, 925). M. J. S.

**Composition of Milk and Milk Products.** By HENRY DROOP RICHMOND (*Analyst*, 1899, 24, 197—201. Compare Abstr., 1897, ii, 511).—The paper deals with a large number (over 29,000) of samples of milk analysed in the laboratory of the Aylesbury Dairy Co. in 1898.

The standards for milk again prove to be fair, as most of the samples were much above the requirements in every constituent; a few gave non-fatty solids so low that, judging by these only, they might have been condemned as containing 5—6 per cent. of water, but it was ascertained that the deficiency was mainly in milk-sugar, the more important constituents—fat, proteids, and ash—being present in normal quantity. No sample which falls a little below the accepted standard should be condemned unless the proteids and ash are also rather low. Vieth's ratio for sugar, proteids, and ash of 13:9:2 was again practically confirmed.

An analysis of cream shows the great variation in the composition of this article, but it seems that the non-fatty solids contain the usual proportion of milk sugar, which fact upsets Storch's evidence for the presence of a new proteid in milk (Abstr., 1897, ii, 420).

Analyses of butter are communicated, showing that the refractive index at 35° varies from 46—47°; a butter prepared in the Channel Islands gave, however, the figure 43·8°.

Interesting analyses are given of so-called "putrid slime," which is in reality a product from milk deposited on the sides of the drum of a separator: *Solids* (of one of the three samples examined), 29·2; *fat*, 1·3; *milk solids*, calculated, 7·2; other *non-fatty solids*, 17·5; *ash*, 3·2, including 1·28 P<sub>2</sub>O<sub>5</sub>. This substance, although also containing any dirt present in the milk, is no doubt largely composed of Storch's mucoid. Its average quantity in milk amounts to about 0·032 per cent. L. DE K.

**Milk Analysis.** By LEONARD DE KONINGH (*Analyst*, 1899, 24, 142—146).—*Analysis of sour milk.*—If this is not too much decomposed, the sp. gr. may be taken with a milk-hydrometer, the sample being previously liquefied by adding 5 c.c. (or more) of a solution of sodium hydroxide of sp. gr. 1·03 to 95 c.c. of the sample. If the sp. gr. of the mixture should differ much from 1·030, a correction should be made by deducting from the gravity found (excess over 1000) 1·5, and dividing the difference by 0·95. As, however, milk loses in gravity by addition of alkali, the author suggests the addition of 0·8 to the gravity obtained. The alkaline milk may be used for the estimation of the fat in the Leffmann-Beam apparatus, allowance being made for the slight dilution.

*Detection of cane sugar.*—As the ordinary non-fatty solids process may fail where cane-sugar has been added to mask the adulteration,

it is suggested that all samples should be tested for cane sugar by a slightly modified form of Cotton's molybdic acid process; 10 c.c. of the milk are mixed with 2 c.c. of a cold saturated solution of pure ammonium molybdate and 8 c.c. of dilute hydrochloric acid (1:8), and the mixture heated for 5 minutes at 80°. A blue coloration is developed if the sample contains 5 per cent. or more of added sugar solution of sp. gr. 1.0308. If the milk is very stale, the test is less satisfactory.

*Detection of boric acid.*—100 c.c. of the sample are heated to boiling in a large beaker covered with a light dish containing cold water; the flame is at once removed and 8 c.c. of dilute nitric acid (1 part of fuming acid diluted to 50 parts) added; the coagulum which forms will occupy about 8 c.c. When cold, the liquid is filtered through muslin, 80 c.c. are collected, and 0.8 gram of dry sodium carbonate added; the whole may now be rapidly evaporated and burnt in a large platinum dish, and the portion soluble in water then tested for boric acid by any recognised process.

L. DE K.

**Possible Source of Error in Modifications of the Leffmann-Beam Method for the Estimation of Fat in Milk.** By HENRY DROOP RICHMOND and F. R. O'SHAUGHNESSY (*Analyst*, 1899, 24, 146—148).—In the original process devised by Leffmann and Beam, the milk was mixed with a solution consisting of equal volumes of amylic alcohol and hydrochloric acid, and finally with sulphuric acid. In a modification of this process devised by Gerber the use of hydrochloric acid is omitted. From the results of a series of experiments the authors conclude that Gerber's method, when carefully practised, generally gives good results, but may at times lead to error, particularly in hot weather. They also show the advisability of first adding the sulphuric acid, next the milk, and then the amylic alcohol. If the acid and amylic alcohol are added first, a mixture is obtained which, when diluted with milk, throws up an amylic compound, by which the layer of fat may become sensibly increased in volume.

L. DE K.

**Estimation of Fat in Milk, using Light Petroleum as a Solvent.** By HENRY DROOP RICHMOND and C. H. ROSIER (*Analyst*, 1899, 24, 172—174).—The authors prefer using light petroleum instead of ether in milk analyses, as it is insoluble in aqueous liquids. To properly extract the fat, the operation should be conducted as follows: 9 c.c. of 91 per cent. sulphuric acid are measured into a tube holding 50 c.c. and constricted just above the point to which 20 c.c. reaches; 10 grams of milk are introduced without mixing it with the acid, and 0.9 c.c. of amylic alcohol is then added, and the whole well shaken. When cooled to 25°, 20 c.c. of light petroleum are added, and the mixture is again thoroughly shaken two or three times. When separation is complete, the petroleum is blown off into a tube containing 20 c.c. of water, with which it is shaken to remove traces of acid; the acid liquid is washed with a little more light petroleum, which is added to the main bulk. The fat solution is finally blown off into a tared flask, and the light petroleum, which should boil

below 80°, is then distilled off and the residual fat dried and weighed. L. DE K.

**Apparatus for Estimating Total Solids and Fat in Milk.** By S. SONN (*Zeit. anal. Chem.*, 1899, 38, 353).—An aluminium boat with a cover is charged with about 2 grams of cotton-wool freed from fat, and is then dried and weighed. Twenty c.c. of the milk are dropped upon the wool, the boat is reweighed and dried in an oven until constant in weight. It is then slipped into a cylindrical metal (nickel-plated) cylinder, closed at the bottom, and furnished with an internal self-starting syphon, the bend of which is a little higher than the upper end of the boat. This cylinder fits loosely into a glass tube, narrowed at its lower end for passing through the cork of the flask in which the fat solution is to be received, and is fitted with a condenser. The extraction proceeds in the same manner as with a Soxhlet extractor, and when it is complete the boat is redried and the amount of fat ascertained from the loss of weight. M. J. S.

**Physical and Chemical Constants of Butter-Fat.** By C. A. BROWNE (*J. Amer. Chem. Soc.*, 1899, 21, 612—633).—The results of a large number of analyses of genuine butter fats are given. The figures include the sp. gr. at 40° (water at 15.5°), the melting point, the acid number, the saponification number, the ether number, the iodine number, the Reichert and Reichert-Meissl numbers, the insoluble acids per cent., the acetyl number, the glycerol, the total and soluble fatty acids, the sp. gr. of the insoluble acids at 20° (water at 20°), the melting point of the insoluble acids, the saponification number of the insoluble acids, the mean molecular weight of the insoluble acids, the sp. gr. of the soluble acids at 20° (water at 20°), the saponification number of the soluble acids, and the mean molecular weight of the soluble acids.

Full particulars as to the methods of determining these constants are given. The results show the great variation in composition of butter-fats, chiefly due to the quality of the cattle food, and many a genuine butter might be condemned as containing margarine; if, however, prepared from the mixed milk of a large herd of cows, there is less danger of this happening.

The author points out the importance of not heating the butter above 50° when preparing the butter-fat for analysis. L. DE K.

**Butter and its Adulterations.** By C. B. COCHRAN (*Chem. Centr.*, 1899, i, 709—710; from *J. Franklin Inst.*, 1898, 147, 85—97).—The author states (compare *Abstr.*, 1898, ii, 198) that in eastern Pennsylvania about 5 per cent. of cotton seed oil (sold under the name of "cream ripener") is added during the churning to increase the yield of butter or rather to make this hold more water. This fraud may be readily detected by the Bechi test. Another fraud now frequently practised consists in melting stale, unsaleable butter and then rechurning the clarified fat with the fresh milk or buttermilk, the resulting product being sold as fresh butter. If otherwise unadulterated, this sophistication may be detected chemically by the high percentage of free acidity and physically by Valenta's acetic

acid test as the critical point or turbidity temperature is lowered from 60° to about 50°; also when applying Jean's modification of this test, the amount of acetic acid required will be raised in the proportion of 7 to 10. The fraud may also be detected microscopically, using polarised light. Fresh butter is amorphous, and the field is dark and even. Butter which has been melted is more or less crystalline, and presents an uneven, spotted field. L. DE K.

**Cryoscopic Examination of Butter and Margarine.** By POURET (*Bull. Soc. Chim.*, 1899, [iii], 21, 738—740).—By the cryoscopic method, using benzene as solvent, the author has determined the molecular weight of various samples of the fat of pure butter and finds that it lies between the limits 631 and 662, whilst that of margarine is practically constant between 840 and 860. A determination of the molecular weight of a sample of butter-fat thus renders it possible to ascertain rapidly whether margarine is present as an adulterant, since 15 per cent. of the latter increases the molecular weight by 30—35 units, an amount greater than the extreme variation observed by the author amongst pure butters. The presence of "vegetaline," the fat obtained from cocoa-nut oil, which is often used to adulterate butter, cannot, however, be detected by this method, as the cocoa-fat has a molecular weight lying within the limits of the values obtained for pure butter-fat. W. A. D.

**Paraffin as an Adulterant of Oleomargarine.** By JOSEPH F. GEISLER (*J. Amer. Chem. Soc.*, 1899, 21, 605—608).—Solid paraffin frequently occurs in margarines; it is added, not to cheapen the article, but to improve its appearance.

Any quantity above 2 or 3 per cent. may be detected as follows: 2.5 grams of the sample are saponified with 20 c.c. of alcohol containing 1 gram of potassium hydroxide, and an equal volume of water is then added; the paraffin will collect on the surface, and may then be further identified. Large quantities will betray their presence by the abnormally low sp. gr. of the sample at 100° F., and by its not giving a clear liquid on saponification.

The fraud may also be detected with the aid of the microscope; two photomicrographs are given in illustration. The author states that no proofs have as yet been brought forward to show that paraffin, even when diluted with butter-fat, is harmless to the system. L. DE K.

**Iodine Absorption of Commercial Tallow.** By ALFRED SMETHAM (*J. Soc. Chem. Ind.*, 1899, 18, 330—331).—The author shares the views of many authorities that the iodine absorption figure offers the most trustworthy method of ascertaining the value of tallow and similar fats for candle or soap making. In using Hübl's test, it is important to use absolute alcohol and to keep the solutions of the iodine and the mercuric chloride separate. As a good deal depends on the length of time of action, the author now allows the iodine to act on the fats for 18 hours.

A table is given showing the iodine absorption figure of a large number of tallows of different kind and origin. L. DE K.

**Saponification Value of Fish-Oils.** By WILHELM FAHRION (*Chem. Centr.*, 1899, i, 645—646; from *Chem. Rev. Fett. Harz-Ind.*, 6, 25—29).—The saponification number of fish oils is not constant. Sardine oil, for instance, gives numbers varying from 185—199, and stickleback oil from 178—210. The saponification may be effected by boiling with alcoholic potash, or in the cold by dissolving in light petroleum and adding alcoholic soda; in this case, it is important to dissolve the soda in absolute alcohol.

Oils with a high iodine number, excepting haddock oil, give too high and irregular results, as they are decomposed by excess of alkali into fatty acids with a lower molecular weight; there is, however, no such danger when the author's method for taking the inner saponification number is used (*Abstr.*, 1898, ii, 654).

Fatty acids may be prevented from undue oxidation, caused by long heating at 100°, by evaporating their solutions in light petroleum to dryness in several platinum dishes and drying the residue for half an hour on the water-bath; in presence of any water, the residue should first be moistened with a little absolute alcohol. L. DE K.

**The Iodine Number of Linseed Oil.** By J. J. A. WIJS (*Chem., Centr.*, 1899, i, 646; from *Chem. Rev. Fett. Harz-Ind.*, 6, 29—31).—The author has determined the iodine number of a large number of linseed oils of undoubted purity and freshness by means of his new process with iodine chloride and acetic acid (*Abstr.*, 1898, ii, 412).

The results of other authors are confirmed as to the quality of the oil varying with the source of the seed. Oil pressed from Dutch seed showed an iodine number of 193—201; from East Indian seed, 182—187; from La Plata seed, 174—182; from North American seed, 177—188; from Baltic provinces, 192—200; from Central Russia, 188—189; from Black Sea districts, 176—182; from Danube districts, 182.

The iodine number increases with the sp. gr. of the sample, which is determined commercially by the aid of Fischer's instrument.

L. DE K.

**Maize Oil (Corn Oil).** By LEONARD ARCHBUTT (*J. Soc. Chem. Ind.*, 1899, 18, 346—347).—The author has tested an authentic sample of maize oil with the following results: Sp. gr., 0.9243 at 15.5°; absolute viscosity, 0.789 at 15.5°; Maumené test using acid containing 97 per cent. of hydrogen sulphate, 81.6°; saponification value, 18.97; iodine absorption figure, 122.7; unsaponifiable matter, 1.69 per cent., and free acid calculated as oleic acid, 2.4 per cent.

From these figures, and also from practical drying tests, it may be concluded that maize oil is a semi-drying oil, rather more strongly drying than cotton seed oil, and that it must be considered unfit for lubricating purposes. L. DE K.

**Composition of the Fatty Oil of Cedar Seeds.** By D. KRYLOFF (*Chem. Centr.*, 1899, i, 592; from *J. Russ. Chem. Soc.*, 1898, 30, 924—926).—A sample of commercial Siberian cedar seed oil, solidified at 20°, had a sp. gr. 0.9326 at 0°/0°, iodine number 149.5—150.5, Reichert-Meißl number 2.0, Hehner number 93.33, saponification

coefficient 191.8, and acid coefficient 1.09. The elaidin test showed the presence of a small quantity of olein. The crystalline acids precipitated from the oil, when purified, melted at  $63^{\circ}$ , and had the composition of palmitic acid; the filtrate, when treated with potassium permanganate by Saytzeff's method (*J. Russ. Chem. Soc.*, 17, 419), yields the tetrahydroxystearic acid melting at  $165^{\circ}$  obtained from linseed oil by Reformatsky, and a substance which melts at  $140^{\circ}$  and is probably dihydroxystearic acid. Cedar seed oil is therefore very similar to linseed, hempseed, and other fatty oils, resembling the first particularly in respect to its content of unsaturated acids. Its content of linoleic acid is about the same as that of the drying oils.

E. W. W.

**Cacao Butter.** By JULIUS LEWKOWITSCH (*J. Soc. Chem. Ind.* 1899, 18, 556—558).—The Reichert-Meissl value of cacao butter has been recorded as 3.52, but the author states that it varies from 0.20 to 0.83. The adulteration with large quantities of cocoa-nut oil or palm-nut oil may therefore be detected by the large increase of volatile soluble fatty acids.

Filsinger has stated that when two grams of cacao butter are dissolved in 6 c.c. of a mixture of 4 parts of ether and 1 part of alcohol, the solution remains clear when cooled to  $0^{\circ}$ , whilst the presence of as little as 5 per cent. of tallow causes crystallisation. The author states that this test is apt to mislead, as some undoubtedly genuine samples deposited crystals at  $9^{\circ}$ , and some even at  $12^{\circ}$ . When the adulteration with tallow has been practised to the extent of more than 10 per cent., the tallow crystals may be readily recognised by the microscope, as they appear like curved tufts somewhat of the shape of an "f," the ends of the *f* resembling horse-tails, whereas cacao butter crystals have the appearance of densely-packed clusters of needles radiating in all directions from a common centre. Unfortunately, when less than 10 per cent. of tallow is present, the tallow crystals lose much of their characteristic appearance.

A better proof of the adulteration with tallow or similar fats is the presence of cholesterol, which is readily isolated and recognised microscopically.

The author also states that although cacao butter does not readily turn rancid if properly kept, it will turn quite as rancid as any other fat under very unfavourable conditions, and it then acquires a nauseous taste and smell.

L. DE K.

**Testing of Oil and Spirit of Mustard.** By JOHANNES GADAMER (*Arch. Pharm.*, 1899, 237, 372—378).—The method previously described (this vol., ii, 455, where *for* 4.5 *read* 4.65), does not always give trustworthy results. It is assumed that the allylthiocarbimide is first converted into allylthiocarbamide,  $\text{CS}\cdot\text{NC}_3\text{H}_5 + \text{NH}_3 = \text{NH}_2\cdot\text{CS}\cdot\text{NHC}_3\text{H}_5$ , from which the silver nitrate then abstracts hydrogen sulphide with formation of silver sulphide and allycyanamide,  $\text{NH}_2\cdot\text{CS}\cdot\text{NHC}_3\text{H}_5 + 2\text{AgNO}_3 + 2\text{NH}_3 = \text{Ag}_2\text{S} + \text{CN}\cdot\text{NHC}_3\text{H}_5$ ;  $2\text{AgNO}_3$  is thus removed from solution for each mol. of thiocarbimide originally present. It is quite possible that some of the compound  $\text{NH}_2\cdot\text{CS}\cdot\text{NHC}_3\text{H}_5$ ,  $\text{AgNO}_3$  (Abstr., 1896, i, 140) may be deposited, and only slowly undergo further decomposi-

tion; if so, only  $1\text{AgNO}_3$  would be removed per mol. of the thiocarbamide as regards a portion of the latter, and this would affect the result of the titration. Now it is conceivable that this source of error might be avoided by using a larger excess of silver nitrate, when the compound  $\text{NH}_2\cdot\text{CS}\cdot\text{NHC}_3\text{H}_5\cdot 2\text{AgNO}_3$  (*loc. cit.*) might be deposited instead, and as this requires  $2\text{AgNO}_3$  per mol. of the thiocarbimide, the titration would not be affected; as a matter of fact, it was found that a larger excess of silver nitrate is beneficial, and the method is to be modified as follows: Of the spirit of mustard, 5 c.c. (= 4.2 grams) are allowed to remain with 50 c.c. of  $N/10$  silver nitrate solution and 10 c.c. of official ammonia solution (German pharmacopœia) for 24 hours in a well stoppered, graduated flask of 100 c.c. capacity, the flask being shaken frequently. After dilution to the mark, 50 c.c. of the clear filtrate, mixed with 6 c.c. of official nitric acid and 1 c.c. of ferric ammonium sulphate solution, must require not more than 17.15 and not less than 16.6 c.c. (16.5) of  $N/10$  ammonium thiocyanate solution to produce a red coloration. This corresponds with 92.5—100 per cent. of  $\text{CS}\cdot\text{NC}_3\text{H}_5$  in the oil.

Experiments with oils from different sources are quoted, and the conclusion is drawn from them that the percentage of sulphur assigned by Grützner (this vol., ii, 530) to the pure natural oil is too low; it is, perhaps, admissible to replace the number 17.15 by 17.2 c.c., in order to allow a somewhat wider margin.

C. F. B.

**Volumetric Estimation of Aniline.** By MAURICE FRANCOIS (*J. Pharm.*, 1899, [vi], 9, 521—524).—The principle of the method depends on the fact that, if bromine water is added to an aniline solution which contains a little sulphate of indigo as indicator, the bromine does not act on the indigo until all the aniline has been converted into tribromaniline. The bromine water (5 grams bromine in 1000 c.c. water) is standardised by means of an aqueous solution of aniline hydrochloride, which contains 1.392 grams of the pure salt in 1000 c.c. (1 c.c. = 0.001 aniline). The bromine water, if exposed to the air, is continually losing bromine; it is therefore essential (1) to use a burette of such capacity that it contains enough bromine water for both the standardisation and estimation without refilling; (2) to close the end of the burette with a plug of cotton wool; (3) to find approximately the number of c.c. of bromine water required, and then, in the final titration, to add nearly the whole at once, in order to avoid the slight loss of bromine which occurs when drops of the solution fall through the air. The method may be applied to solutions containing aniline or its hydrochloride, the presence of ammonium chloride does not vitiate the result, and, finally, if the solution to be titrated contains mineral substances which would react with the bromine, the aniline may be liberated by potash and distilled in steam. The degree of dilution of the aniline solution does not influence the result.

H. R. LE S.

**Volumetric Estimation of Alkaloids.** By ELIÉ FALIÈRES (*Compt. rend.*, 1899, 129, 110—111).—The estimation of alkaloids by titration with an acid is in many cases unsatisfactory, because the colour

change of the indicator is not sharply defined, and also is more or less masked when, as is often the case, the alkaloidal solutions are coloured. To obviate these and other difficulties which are experienced when ordinary indicators are used, the author employs an ammoniacal solution of copper as indicator; the point of neutralisation is then made evident, not by a colour change, but by the precipitation of copper oxide, which is most readily seen. The copper solution is prepared by dissolving 10 grams of copper sulphate in about 500 c.c. of water, adding ammonia until the precipitate first formed is nearly all dissolved, filtering, and diluting to a litre. This solution is titrated by means of decinormal sulphuric acid. For an estimation, 0.1 gram of the alkaloid is dissolved in 20 c.c. of decinormal sulphuric acid, the flask placed on a black surface, and the ammoniacal copper solution added until there is a persistent turbidity in the liquid. The volume of copper solution used corresponds with the amount of sulphuric acid uncombined with the alkaloid, and, therefore, the amount of acid combined with the alkaloid is readily calculated. In estimating the total alkaloids in cinchona bark by this method, the colouring matter need not be removed before titration.

H. R. LE S.

**A New Method for the Estimation of Morphine in Opium.** By HARRY M. GORDIN and ALBERT B. PRESCOTT (*Arch. Pharm.*, 1899, 237, 380—384).—The method described previously (this vol., i, 90) has been modified in so far that the maceration of the drug with the ammoniacal mixture is continued for 5—6 instead of 3 hours, and the evaporation of the liquid is effected at the ordinary temperature in a good draught. Further, the morphine is extracted by percolation with a mixture of chloroform and absolute alcohol (5 : 1 by volume) instead of with acetone, and the evaporation of the solvent is again effected in a good draught; an excellent percolator for this purpose is obtained by cutting off the upper  $\frac{3}{5}$  of a 50 c.c. burette, and using the lower part with a plug of cotton-wool placed above the stopcock.

An alkalimetric estimation may also be employed, either alone or combined with the iodometric one. In this case, 3 grams of the drug are treated just as in the other method up to the evaporation of the chloroform-alcohol mixture. The residue of morphine is then ground with 50 c.c. of  $N/20$  sulphuric acid, and rinsed with water into a tall, narrow measuring cylinder, the whole diluted to 90 c.c., shaken, and allowed to settle for a time, after which 75 c.c. are filtered into a beaker and mixed with 30 or 35 c.c. of  $N/20$  caustic potash, the excess of the latter being titrated finally with  $N/20$  acid; the number of c.c. of acid neutralised by the morphine, multiplied by 0.568, gives the percentage of morphine in the opium. The indicator used is filter paper, dyed a pale yellow with neutral methyl-orange solution, and it is dipped for about 10 seconds in the liquid; the acid and alkali must be standardised under conditions similar to those of the estimation. If it is desired to control the result by an iodometric estimation, the titrated liquid is mixed with 3—4 grams of calcium hydroxide, diluted to 250 c.c., and shaken vigorously and frequently during an hour; 50 c.c. are then filtered into a 100 c.c. graduated flask, acidified, treated with excess of  $N/10$  iodine solution, and titrated with thiosulphate,



just as described in the previous paper; the weight of iodine used, multiplied by 150, gives the percentage of morphine.

In a sample of opium 17.66—17.90 per cent. of morphine were found by the alkalimetric and 17.49—17.50 by the iodometric method, but by the gravimetric method only 14 per cent. were found.

C. F. B.

**Separation of Brucine from Strychnine.** By WILLEM STOEDER (*Chem. Centr.*, 1899, i, 506; from *Ned. Tydschr. Pharm.*, 11, 1—5).—The separation of brucine from strychnine by means of potassium ferrocyanide in a sulphuric acid solution is untrustworthy. Good results are obtained by Keller's method (*Abstr.*, 1894, ii, 491). The crude alkaloids, weighing about 0.3 gram, are dissolved in 10 c.c. of 10 per cent. sulphuric acid, 1.5 c.c. of 50 per cent. nitric acid is added, and the mixture left for  $1\frac{1}{2}$  hours. The brucine is thus converted into dinitrobrucine, and the strychnine may be recovered by agitating the liquid with chloroform, after rendering alkaline with ammonia.

L. DE K.

**A New Test for Cocaine.** By GEORGE L. SCHAEFER (*J. Amer. Chem. Soc.*, 1899, 21, 634—635).—The following test is suggested for detecting the presence of the other coca alkaloids in cocaine, and is preferable to McLagan's permanganate test.

0.05 gram of the commercial cocaine hydrochloride is dissolved in 20 c.c. of water, mixed first with 5 c.c. of a 3 per cent. solution of chromic acid, and then with 5 c.c. of a 10 per cent. solution of hydrochloric acid, and the solution cooled to 15°. If the sample is pure, a clear solution will result, but if more than traces of the other coca alkaloids are present, the solution becomes cloudy at once, or in a few minutes.

L. DE K.

**Reactions of Indole Bases and of Proteids.** By JULIUS GNEZDA (*Compt. rend.*, 1899, 128, 1584—1587).—On fusing oxalic acid with a trace of indole, a sublimate and residual mass of a splendid purple colour are obtained, and on dissolving in water, a coloured solution is formed which is only slightly changed by the addition of potash; 2'-methylindole, scatole, and 1'-methylindolecarboxylic acid behave similarly, whilst 2'-phenylindole gives a greenish-yellow sublimate, changing to black. Phthalic, isophthalic, or terephthalic acid, when fused with indole, 2'-methylindole, scatole, or 1'-methylindolecarboxylic acid, yields a faintly violet sublimate; 2'-phenylindole is coloured green and violet by phthalic and terephthalic acids respectively, but gives no colour with isophthalic acid. Malonic, succinic, and glutaric acids give slightly red products with indole, 2'-methylindole, scatole, and 1'-methylindolecarboxylic acid, the intensity of the coloration diminishing as the number of  $\text{CH}_2$ -groups increases.

On adding albumin, peptones, or gelatin to fused oxalic acid, a pinkish sublimate is obtained; green colorations are formed with glycocholic, taurocholic, and cholic acids, and with bilirubin, whilst with other substances of animal origin such as leucine, tyrosine, the xanthine bases, urea, neurine, glycocine, sugars, &c., indefinite brownish-

yellow products are formed. Alloxanthin gives a characteristic red colour with fused oxalic acid.

Proteids give faint orange colorations with malonic, succinic, glutaric, and the phthalic acids, and the latter give slightly yellow masses with cholic acid.

Scatole, 1'-methylindolecarboxylic acid, and an alcoholic solution of indole, give orange colorations with hydrofluoric acid, whilst 2'-phenylindole is turned slightly yellow, and 2'-methylindole violet; hot hydrofluosilicic acid acts similarly. A very persistent red colour is obtained on heating hydrofluosilicic acid with a concentrated solution of peptone, gelatin, or albumin; the albumin must be heated until peptonisation is complete.

When albumin (white of egg) is subjected to prolonged treatment with concentrated hydrochloric acid, the products formed give characteristic indole reactions.

T. H. P.

**Detection of Albumin in Urine.** By GABRIEL GUÉRIN (*J. Pharm.*, 1899, [vi], 9, 576).—A 10 per cent. aqueous solution of di-iodoparaphenolsulphonic acid (sozoiodol) is a very delicate reagent for the detection of albumin in urine. 10—15 drops of the reagent when added to 8 or 10 c.c. of the filtered urine produce a whitish, flocculent precipitate or a milky turbidity if albumin is present. Albumoses, peptones, and most alkaloids are also precipitated by it, but their precipitates readily dissolve on heating, whereas that produced by albumin is completely insoluble. Alkaline urates and uric acid are not precipitated by this reagent.

H. R. LE S.

**Estimation of Albumoses and Peptones.** By JEAN EFFRONT (*Bull. Soc. Chim.*, 1899, [iii], 21, 680—683).—The method of analysis is based on the author's observations on the influence of acidity on the solubility of proteoses in alcohol (this vol., i, 835). 50 c.c. of a 5 per cent. solution of the crude peptone are neutralised with *N*/10 sodium hydroxide, left for 2 hours, and the precipitate of syntonin washed with water and alcohol, dried at 100°, and weighed. Another 50 c.c. of the 5 per cent. solution are neutralised with normal caustic soda, diluted with water to 55 c.c., and filtered after some time; 44 c.c. of the filtrate, corresponding with 40 c.c. of the original solution, are mixed with 8 c.c. of normal hydrochloric acid and 250 c.c. of 95 per cent. alcohol, the clear alcoholic solution is neutralised by adding 8 c.c. of normal soda, and the precipitated albumoses are finally collected and dried at 100°. The peptone, together with mineral matter, is obtained by evaporating the filtrate. The application of this process to the products of the peptic digestion of fibrin at various stages shows that it yields accurate and consistent results; it is also very expeditious.

N. L.

## General and Physical Chemistry.

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**Refractive Indices and Densities of Normal and Semi-normal Aqueous Solutions of Hydrogen Chloride and the Chlorides of the Alkalis.** By SIR JOHN CONROY (*Proc. Roy. Soc.*, 1899, **64**, 308—318).—A number of refractive indices have been determined by the hollow prism method, special care being taken to keep the temperature of the prism at 18°; this was effected by a water jacket which was in contact with the prism above, below, and, as far as possible, on the faces.

The refractive indices and densities of normal and semi-normal solutions of the chlorides of hydrogen, lithium, sodium, potassium, and rubidium increase, as a rule, with the molecular weight; solutions of potassium chloride are exceptional, for their indices are less than those of the corresponding sodium chloride solutions. It is shown that whilst a litre of a normal solution of hydrogen, lithium, or sodium chloride contains nearly the same weight of water, a litre of a normal solution of potassium chloride contains about 10 grams less water than a litre of normal sodium chloride solution. Thus the water in a normal potassium chloride solution may be regarded as less dense than in a normal sodium chloride solution. Allowing for this decrease of density, the difference between the refractive indices of water thus calculated and the observed refractive indices of the solutions increases regularly with the molecular weight, potassium chloride no longer being an exception. The increase, however, has no apparent relation to the increase of molecular weight.

The change of the refractive index with temperature has been determined for the above solutions between 10° and 20°. J. C. P.

**Simple Method of Reversing the Sodium Spectrum.** By H. KREUSLER (*Chem. Zeit.*, 1899, **23**, 37).—When a sodium chloride bead is held in the flame, a small dark "aureole" is observed just above the glowing bead, and as this aureole consists of dense sodium chloride vapour at a relatively low temperature, it may readily be employed for absorption. A piece of platinum wire is bent in such a way as to form two double loops, the lower parts of which hold beads of sodium chloride, whilst the upper and larger parts serve to increase the space occupied by the sodium chloride vapour. The whole is held with the beads hanging downwards in the flame of a spirit lamp, placed between an Auer's burner and the spectroscope, and is so arranged that the beads cover one another in the field of vision. In the upper half of the spectrum, the sodium lines are observed as extremely bright, in the lower half as dark lines. J. J. S.

**Spectrum of the Corona.** By SIR NORMAN LOCKYER (*Proc. Roy. Soc.*, 1899, **64**, 168—170).—According to Nasini, the spectrum of the gases collected at the solfatara of Pozzuoli probably contains the characteristic green line of the corona. This and one of the other chief lines of the spectrum of the corona appear to coincide with

enhanced lines of iron. It is doubtful, however, whether this coincidence is real, because the other lines in the corona are not coincident with enhanced iron lines. Careful examination of eclipse photographs obtained in 1893, 1896, and 1898 shows, in fact, that the coincidence is only approximate, and that the lines in question probably belong to some undiscovered gas or gases. J. C. P.

**Chemical Classification of the Stars.** By SIR NORMAN LOCKYER (*Proc. Roy. Soc.*, 1899, 65, 186—191).—Comparison of stellar spectra with those of numerous elements at different temperatures (compare Abstr., 1898, ii, 2) has led to a classification of stars according to their temperature, the order of temperature being deduced from the character of their spectra. The hottest stars have the simplest chemistry, and in a series of stars from the highest temperatures to the lowest, the chemical forms indicated by the spectra become gradually more complex. On the idea that in this increasing complexity of stellar chemical forms an inorganic evolution may be traced similar to the organic evolution shown by successive geological strata, stars have been divided into a number of genera, the form of terminology being analogous to that adopted in geological classification. The simplest types are supplied by the proto-hydrogen and cleveite-gas stars, proto-hydrogen being that form of hydrogen which gives enhanced lines (*loc. cit.*); as the temperature falls, the stars are of the order proto-metallic or metallic, and the lowest temperature stars have fluted spectra. J. C. P.

**Presence of Oxygen in the Atmospheres of certain Fixed Stars.** By DAVID GILL (*Proc. Roy. Soc.*, 1899, 65, 196—206).—The spectra of  $\beta$  Crucis,  $\beta$  and  $\epsilon$  Canis Majoris and probably  $\beta$  Centauri are all practically identical, and contain, in addition to the hydrogen and helium lines, the stronger oxygen lines, a probable magnesium line, a probable carbon line, and three unknown strong lines. J. C. P.

**Specific Rotatory Power and Position Isomerism.** By PHILLIPE A. GUYE and A. BABEL (*Chem. Centr.*, 1899, i, 466; from *Arch. Sci. phys. nat. Genève*, [iv], 7, 23—42).—The specific rotatory powers of substituted derivatives of amylic benzoate and of aniline have been determined, and the influence of the substituent studied. The amylic benzoate derivatives are liquid, and were examined in the pure state; the aniline derivatives were examined in solution. The amylic alcohol used in the preparations had  $[\alpha]_D -4.4^\circ$  to  $-4.5^\circ$ .

*Amylic orthonitrobenzoate*, b. p.  $238^\circ$  under 69 mm. pressure, sp. gr. 1.135 at  $17^\circ$ ,  $n_D$  1.5132,  $[\alpha]_D -0.61^\circ$  at  $17^\circ$ ,  $+0.90^\circ$  at  $75^\circ$ ; *metanitrobenzoate*, b. p.  $223-225^\circ$  under 52 mm. pressure, sp. gr. 1.144 at  $19^\circ$ ,  $n_D$  1.5187,  $[\alpha]_D +5.85^\circ$  at  $19^\circ$ ,  $+4.28^\circ$  at  $75^\circ$ ; *paranitrobenzoate*, b. p.  $250-252^\circ$  under 80 mm. pressure, sp. gr. 1.140 at  $17^\circ$ ,  $n_D$  1.5203,  $[\alpha]_D +6.93^\circ$  at  $17^\circ$ ,  $+4.82^\circ$  at  $75^\circ$ ; *orthobromobenzoate*, b. p.  $285-287^\circ$  under 730 mm. pressure, sp. gr. 1.279 at  $16^\circ$ ,  $n_D$  1.5243,  $[\alpha]_D +1.88^\circ$  at  $16^\circ$ ,  $+1.43^\circ$  at  $75^\circ$ ; *metabromobenzoate*, b. p.  $286-289^\circ$  under 737 mm. pressure, sp. gr. 1.285 at  $17^\circ$ ,  $n_D$  1.5243,  $[\alpha]_D +2.70^\circ$  at  $16^\circ$ ,  $+1.99^\circ$  at  $75^\circ$ ; *parabromobenzoate*, b. p.  $287-290^\circ$  under 724.3 mm. pressure, sp.

gr. 1.288 at 16°,  $n_D$  1.5282,  $[\alpha]_D + 3.18^\circ$  at 16°,  $+ 2.35^\circ$  at 75°; *orthamidobenzoate*, b. p. 192—194° under 41 mm. pressure, sp. gr. 1.047 at 17°,  $n_D$  1.5364,  $[\alpha]_D$   $5.98^\circ$  at 17°,  $+ 4.99^\circ$  at 75°; *metamidobenzoate*, b. p. 184—187° under 35 mm. pressure, sp. gr. 1.051 at 18°,  $n_D$  1.5351,  $[\alpha]_D + 4.95^\circ$  at 18°,  $+ 4.30^\circ$  at 75°; *paramidobenzoate*, m. p. 27—30°, b. p. 215° under 35 mm. pressure, sp. gr. 1.050 at 75°,  $n_D$  1.5369 at 75°,  $[\alpha]_D + 4.19^\circ$  at 75°; *metatoluate*, b. p. 266—268° under 725 mm. pressure, sp. gr. 0.976 at 20°,  $n_D$  1.4929,  $[\alpha]_D + 5.05^\circ$  at 20°.

The following derivatives of aniline and toluidine were examined in 5 per cent. pyridine solution. *Tartaryl anilide*, m. p. 250°, with decomposition,  $[\alpha]_D + 259^\circ$ ; *orthotoluidide*, m. p. 200°, with decomposition,  $[\alpha]_D + 239^\circ$ ; *metatoluidide*, m. p. 182°, with decomposition,  $[\alpha]_D + 233^\circ$ ; *paratoluidide*, m. p. 230°, with decomposition,  $[\alpha]_D + 239^\circ$ .

The rotatory powers of the following derivatives of valeric acid were determined in 10 per cent. alcoholic solution. The valeric acid used in their preparation had  $[\alpha]_D + 11.12^\circ$  at 15°. *Valeryl anilide*, m. p. 95—96°,  $[\alpha]_D + 10.5^\circ$ ; *orthotoluidide*, m. p. 68—70°,  $[\alpha]_D + 9.3^\circ$ ; *metatoluidide*, m. p. 60—61°, no appreciable rotation; *paratoluidide*, m. p. 69—71°,  $[\alpha]_D + 19.1^\circ$ .

The following malic acid derivatives were examined in 5 per cent. pyridine solution. *Malyl anilide*, m. p. 198°,  $[\alpha]_D - 101.1^\circ$ ; *orthotoluidide*, m. p. 179°,  $[\alpha]_D - 61.8^\circ$ ; *metatoluidide*, m. p. 153°,  $[\alpha]_D - 75.9^\circ$ ; *paratoluidide*, m. p. 206°,  $[\alpha]_D - 92.5^\circ$ .

In all cases except that of amylic orthonitrobenzoate, the rotatory power falls with rising temperature. The molecular refractions of the compounds investigated are a little higher than the values calculated with the help of Conrady's coefficient. The molecular volumes of the amylic benzoate derivatives are all higher than the values calculated according to I. Traube.

J. C. P.

**Specific Rotatory Power and Position Isomerism.** By PHILLIPE A. GUYE and A. BABEL (*Chem. Centr.*, 1899, i, 812, from *Arch. Sci. phys. nat. Genève*, [iv], 7, 109. Compare preceding abstract). A review of the determinations of the rotation of amylic salts derivatives of tartaric, malic, valeric, and methyladipic acids, menthol, and *d*-carboxime leads to the following conclusions. If the influence on rotation of mono- and di-derivatives of benzene is compared, the following order is obtained: ortho-compound—phenyl group—meta-compound—para-compound. Following this order, the rotation may steadily increase, decrease, or pass through a maximum or minimum, and these results accord with those obtained by Frankland and Wharton (*Trans.*, 1899, 75, 337).

L. M. J.

**Relations between Optical Isomerism and Triboluminescence.** By AMERIGO ANDREOCCHI (*Gazzetta*, 1899, 29, i, 516—519).—From the results of an examination of santonin derivatives the author draws the following conclusions. 1. Two optical isomerides which are antipodes show the same behaviour as regards triboluminescence. 2. Crystals of racemic forms do not exhibit triboluminescence even though they may be derived from triboluminescent forms. 3. Optically active isomerides which are not antipodes do not behave similarly with respect to triboluminescence. 4. Optically

active double forms, resulting from two non-antipodal components, may be triboluminescent.

With these compounds, the triboluminescence diminishes as the crystals are reduced more and more to a fine state of division and also those substances which are strongly triboluminescent possess to a marked degree the properties of superfusion and supersaturation and pass very slowly from the amorphous to the crystalline condition.

T. H. P.

**The Latent Photographic Image.** By R. ED. LIESEGANG (*Chem. Zeit.*, 1899, 23, 4—5).—Support is given to the view that, on exposure to light, part of the silver bromide becomes transformed into bromine and a lower bromide (argentic bromide,  $\text{Ag}_2\text{Br}$ ). On development, this lower bromide becomes completely reduced to metallic silver, and, in order to account for the very large amount of silver thus formed compared with the minute quantities of argentic bromide which can be present on the exposed plate, the following hypothesis is advanced. The silver formed during development from the argentic bromide, is in a "nascent state" and immediately reacts with the argentic bromide, yielding a further quantity of the lower bromide, which, in the presence of the developer, again yields nascent silver. The reaction can thus proceed until the argentic bromide under the exposed parts becomes more or less completely reduced to metallic silver.

J. J. S.

**Hydrogen Peroxide as the Active Agent in producing Pictures on a Photographic Plate in the Dark.** By WILLIAM J. RUSSELL (*Proc. Roy. Soc.*, 1899, 64, 409—419).—Hydrogen peroxide acts on a photographic plate in the dark in exactly the same way as certain metals and organic compounds. A photographic plate laid on a dish containing pure water is not affected until a trace of hydrogen peroxide is added, when the plate rapidly darkens. The interposition of substances which are opaque to the action of the metals and terpenes prevents also any action by hydrogen peroxide, whilst the same substances are transparent to the action in both cases. The metals that act most strongly on a photographic plate are those which decompose water most readily; thus the formation of hydrogen peroxide can be accounted for, and even demonstrated, by laying a moistened piece of Wurster's tetramethylparaphenylenediamine paper on the bright metal surface. Practically the terpenes are the only organic compounds which act on a photographic plate, and the oxidation of this class of compounds gives rise to hydrogen peroxide. The ordinary essential and vegetable oils are all more or less active, whilst the mineral oils and compounds like benzene, naphthalene and methylic alcohol produce no effect.

A weak solution of hydrogen peroxide acts on a photographic plate even though gelatin, celluloid, gutta-percha tissue, indiarubber, tracing paper, goldbeater's skin, &c., be interposed, the time required for the action increasing rapidly with the thickness of the intervening layer; the action at first is almost *nil*, and only gradually reaches its maximum effect. When a sheet of the thinnest gelatin was placed over a weak hydrogen peroxide solution, and a plate was laid on the

gelatin, successive exposures of twenty minutes each produced photographic impressions of gradually increasing intensity. The hydrogen peroxide requires time to travel through the intervening inactive substance, and the latter may in this way become active and of itself produce an impression on a photographic plate.

The transmission of the action through an inactive substance is greatly assisted by moisture; much less time was required for the production of a picture when the intervening inactive substance was damp. Alcohol also was found to accelerate the transmission of the action.

Several liquids, such as alcohol, ethylic acetate, and chloroform, produced no effect on a photographic plate even after a week's exposure, but when they had been in contact with polished zinc foil, they became active and produced a picture after a short exposure. It was found, however, that the zinc effected this change only when the liquids in question contained a trace of moisture. Perfectly dry specimens remained inactive even after a week's contact with zinc.

The observations show that hydrogen peroxide is the active agent in all the phenomena dealt with. J. C. P.

**Electromotive Force of some Concentration Batteries and of a Copper-Zinc Battery with Organic Solvents.** By ROBERTO SALVADORI (*Gazzetta*, 1899, 29, i, 498—500).—A cell consisting of a copper and a zinc plate immersed in a solution of hydrogen chloride or trichloroacetic acid in benzene or ether gives no E.M.F., although the zinc is strongly attacked and much hydrogen evolved. The following table gives the E.M.F. obtained on using other solvents:

Solvent.	Hydrogen chloride.		Trichloroacetic acid.	
	Concentration.	E. M. F.	Concentration in grams per 100 of solution.	E. M. F.
Water .....	{ —	—	6.65	0.830
Methylic	{ N/20	0.838	1.50	0.765
	{ N/10	0.633	6.31	0.811
alcohol	{ N/20	0.608	1.12	0.877
Ethylic	{ N/10	0.537	4.29	0.771
	{ N/20	0.605	1.07	0.735
alcohol	{ N/10	0.409	5.90	5.573
	{ N/20	0.410	0.95	0.495 to 0.529*
Acetone .....				

A table is also given of the E.M.F. of cells containing two zinc rods immersed in different solutions of potassium chloride, the solvents for the latter being water and methylic or ethylic alcohol. In general, the E.M.F. obtained in this way are very small, the largest being with equally concentrated aqueous and ethylic alcoholic solutions of potassium chloride. T. H. P.

**Practical Utility of Semi-permeable Membranes.** By B. MORITZ (*Chem. Zeit.*, 1899, 23, 400—401).—Notwithstanding their importance in physico-chemical investigations, semi-permeable mem-

\* One minute after immersing the electrodes.

branes have found but little application in practical work. In many cases, however, the author considers they might be usefully employed, and, as examples, suggests the separation, at least qualitatively, of many organic compounds, and the concentration of solutions of unstable compounds. They might also be employed for the determinations of the value of glues and other compounds, which alter on exposure to air, as such alteration would, in all probability, be accompanied by changes in the osmotic pressure.

L. M. J.

**Electrolytic Potential.** By A. SCHÜKAREFF (*Zeit. physikal. Chem.*, 1899, 29, 726—729).—The consideration of the electrolytic properties of solutions may be simplified by the idea of an 'electrolytic potential' which may be defined as the work required to alter the conductivity by unity. On the assumption that the change of electrolytic potential is proportional to the change of chemical potential, the author deduces the equation,  $\lambda^2/v = \text{constant}$ , for the effect of dilution on conductivity, a result which is valid for very weak electrolytes.

L. M. J.

**Electrical Conductivity and Luminosity of Flames containing Vaporised Salts.** By ARTHUR SMITHELLS, H. M. DAWSON, and HAROLD A. WILSON (*Proc. Roy. Soc.*, 1898, 64, 142—148).—According to Arrhenius, the conduction of an electric current in flames containing vaporised salts is electrolytic in character; the authors' experiments confirm this view, although the electrolytic conduction is different in some respects from that in aqueous solution; Ohm's law, for example, is obeyed only within certain limits.

The conductivity of a vaporised salt increases very rapidly with the temperature. The conductivities of different salts vary with the electropositive constituent, and for various salts of the same metal equivalent solutions sprayed into the flame give equal conductivities, provided the concentration be not too great. The conductivity of the haloid salts as a group is distinct from that of the oxy-salts; the conductivities of the latter are approximately equal, and approach those of the hydroxides. The conductivity of acids is small compared with that of the alkali salts. The introduction of chloroform vapour into a coloured flame and the consequent decolorisation of the flame does not lead to any appreciable decrease of conductivity, so that the colour of a flame produced by a vaporised salt cannot be due, like the conductivity, to the ionisation of the salt; it must be attributed to a chemical process in which the metal is set free, probably to a process of reduction by the flame gases.

The view of Arrhenius that vaporised salts are hydrolysed by the water vapour in the flame, and that the hydroxide then furnishes the ions, is not borne out by experiments made with a cyanogen instead of a coal-gas flame; the presence of water does not seem necessary for the formation of ions.

J. C. P.

**Electrical Conductivity of Flames containing Salt Vapours.** By HAROLD A. WILSON (*Proc. Roy. Soc.*, 1899, 65, 120—123. Compare preceding abstract).—When two platinum gauze electrodes are



placed in a flame into which a salt solution is sprayed, the current attains a nearly constant value as the E.M.F. increases, provided both electrodes are hot. The current is much greater when the negative electrode is hot and the positive electrode cool, than when the negative electrode is cool and the positive one hot; the fall of potential near a cool electrode is nearly equal to the total fall of potential, especially if that electrode be the negative one.

Nearly all the ionisation of the salt vapour takes place at the surface of the electrodes, and the contact of fresh vapour with the electrodes, especially the negative one, produces a marked increase of current.

The relative velocities of ions in the flame were estimated from the potential fall required to urge the ions against the upward current of gases. In this way, it was found that the positive ions Li, Na, K, Rb, and Cs have nearly the same velocity, whilst the negative ions of various salts of these metals have a velocity about seventeen times as great. The fact that the ionisation of the salts takes place only at the surface of the electrodes, combined with the greater velocity of the negative ions, accounts naturally for the phenomena of unipolar conduction. J. C. P.

**Electrolytic Precipitation of Metals on Electrodes of Platinum Gauze.** By CLEMENS WINKLER (*Ber.*, 1899, **32**, 2192—2194).—A piece of platinum gauze (weighing 10 grams per sq. cm., containing 250 meshes to the sq. cm., and made of wire 0.12 mm. thick), 10.5 cm. long and 5.5 cm. wide, has its long edges turned over a little, to give it additional strength, a lead of stout platinum wire riveted to it in the centre, and is then bent into a cylinder 5 cm. high and 3.5 cm. in diameter, a slit being left to admit the anode wire. This is used instead of the ordinary cathode of platinum foil; the precipitated metals adhere to it much more firmly than to foil, and the precipitation can be effected with a much greater current-density, and therefore in much less time (as little as one-fourth of the time with a cathode of platinum foil); by its means also, copper may be precipitated, without any tendency to fall off, from a solution acidified with sulphuric acid.

A cathode of brass wire gauze has already been employed by Paweck (*Österreich. Zeit. Berg.-Hüttenwesen*, **46**, 570). C. F. B.

**Dissolution of an Iron Anode in a Solution of Sodium Acetate and Acetic Acid.** By GEORGES ARTH (*Bull. Soc. Chim.*, 1899, [iii], **21**, 766—768).—When an aqueous solution containing 5 per cent. of sodium acetate and 5 per cent. of acetic acid is electrolysed between a pure iron anode and a platinum cathode, using a feeble current at a low voltage, the iron dissolves as ferrous acetate in an amount corresponding with that required by Faraday's law. At higher voltages, and under certain conditions, which have not yet been accurately determined, the metal assumes an almost "passive" condition, and only a small quantity of ferric acetate is formed. In other experiments, the theoretical amount of iron was dissolved as ferric acetate, a small quantity of ferrous salt being also produced. The work of Wohlwill on univalent and trivalent gold ions is

referred to in connection with these results (*Zeit. Elektrochem.*, 1897, 4, 379, 402, 421). N. L.

[NOTE BY ABTRACTOR.—The similar behaviour of chromium has been noticed by W. Hittorf (compare Abstr., 1898, ii, 363; also *Zeit. Elektrochem.*, 1899, 6, 6—10).]

**Dissociation Equilibrium of Strong Electrolytes.** By HANS EULER (*Zeit. physikal. Chem.*, 1899, 29, 603—612).—Noyes considers the departures from Ostwald's dilution law in the case of strong electrolytes to be due to the fact that determinations of dissociation by the conductivity method are untrustworthy (Abstr., 1893, ii, 1143), whilst Arrhenius regards these as correct, but the mass-action law as inapplicable to such cases. Jahn has pointed out that the dissociation determinations assume the constancy of the ion-velocities at all dilutions (Abstr., 1899, ii, 6); but the author considers that this cannot be the cause of the discrepancies, which frequently occur for dilutions higher than  $N/5$ , above which the viscosity and the ion-friction are practically constant. Storch has given a general form of dilution law in which the exponent (which in Ostwald's law equals 2, and in Rudolphi's law is 1.5) varies for different salts (Abstr., 1896, ii, 288), and the author has determined this exponent for a large number of salt solutions, for which it varies from 1.4 to 1.7. The values change but slightly with temperature, a small decrease with rise of temperature being observed, so that the discrepancies are not due to polymerisation of the solvent, and the author does not consider the electrostatic attraction of the ions to be a possible cause. The most probable cause is finally considered to be an alteration of the dissociative power of the solvent, consequent on the presence of the dissolved salt (compare Abstr., 1899, ii, 492). L. M. J.

**Alteration of Free Energy in Melted Halogen Compounds of some Metals.** By OSKAR H. WEBER (*Zeit. anorg. Chem.*, 1899, 21, 305—360).—This work, which necessitates the determination of the E.M.F. of cells with molten salts, is essentially similar to that of Czepinski (this vol., ii, 267), but the determinations have been carried to higher temperatures and with improved apparatus. The E.M.F. of the chain  $\text{Pb} \mid \text{PbCl}_2 \mid \text{Cl}$  was determined between 502° and 956°, the latter being the boiling point of the salt. It was found that the temperature coefficient was practically constant from the melting point (506°) to about 900°, so that between these limits the alteration of total energy, that is, the heat development, is practically constant (*loc. cit.*), and, further, that the heat capacity of the compound is equal to the sum of the heat capacities of the components. By subtraction of the external work, the heat development is obtained which should be directly comparable with that determined directly, the differences are very slight and do not reach 0.5 per cent. From the heat produced above and below the melting point, the value 5.607 Cal. is obtained for the latent heat of fusion of lead chloride, a number in accord with Rudberg's direct determination, 5.806 Cal. Czepinski found that above 650° a very rapid fall of E.M.F. occurs, and this is due to the backward diffusion of the lead and chlorine; in the author's experiments, this does not occur until about 900°, owing to the improved

form of the electrolytic tube. With lead bromide, analogous results were obtained, but the agreement with thermochemical determinations is not so satisfactory. The melting and boiling points were found to be  $490^{\circ}$  and  $918^{\circ}$  respectively, and the latent heat of fusion  $5.1$  Cal. (direct determinations =  $4.5$  Cal.). Similar chains, with silver chloride and silver bromide, were examined; in the latter case, two sets of values were obtained, abnormal results being found for two or three readings, but as the E.M.F. again became normal, this appeared to be due to the action of the molten salt on the porcelain. The latent heat of fusion of silver chloride was calculated to be about  $4.4$  Cal. The chain with cadmium chloride is interesting, as at the higher temperatures both cadmium and chlorine are gaseous; the melting and boiling points of the salt were found to be about  $568^{\circ}$  and  $964^{\circ}$  respectively, and the boiling point of cadmium about  $780^{\circ}$ . The value for the latent heat of fusion of the salt is  $10.5$  Cal., a number which is apparently high; the latent heat of vaporisation of cadmium is  $26$  Cal., and this is probably very nearly correct. Cadmium bromide was examined to  $860^{\circ}$ , and the latent heat of fusion found to be  $5.0$  Cal. The following are the values of the E.M.F.'s found for these chains:  $\text{Pb} \mid \text{PbCl}_2 \mid \text{Cl}$ ,  $1.2818 - 0.0_3584 (t - 506)$ ;  $\text{Pb} \mid \text{PbBr}_2 \mid \text{Br}$ ,  $1.0571 - 0.0_3500 (t - 490)$ ;  $\text{Ag} \mid \text{AgCl} \mid \text{Cl}$ ,  $0.8848 - 0.0_3270 (t - 650)$ ;  $\text{Cd} \mid \text{CdCl}_2 \mid \text{Cl}_2$ ,  $1.3680 - 0.0_3580 (t - 590)$ ,  $\text{Cd} \mid \text{CdBr}_2 \mid \text{Br}$ ,  $1.1319 - 0.0_3486 (t - 610)$ , the cadmium values being only for temperatures below  $780^{\circ}$ . Chains of the Daniell type were also examined with lead and silver electrodes at temperatures from  $500^{\circ}$  to  $1000^{\circ}$ ; the values agree fairly with those calculated from the previous chains, and indicate for both metals a greater dissociation in the chloride than in the bromide.

L. M. J.

**Ratio of the Specific Heats in some Gaseous Saturated Hydrocarbons.** By A. DANIEL and PAUL PIERRON (*Bull. Soc. Chim.*, 1899, [iii], 21, 801).—Determinations by Kundt's method of the ratio of the two specific heats for ethane ( $1.225$ ), propane ( $1.153$ ), and isobutane ( $1.108$ ) gave the values indicated. In the case of ethane, Clément and Desormes' method was also employed, the value  $1.213$  being obtained.

N. L.

**Specific Heats of Gases and Mechanical Equivalent of Heat.** By ANATOLE LEDUC (*Ann. Chim. Phys.*, 1899, [vii], 17, 484—510).—A thermodynamical paper not suitable for abstraction.

G. T. M.

**Acoustical Method for the Determination of the Melting Point of Fats and Waxes.** By EDWIN DOWZARD (*Chem. News*, 1899, 79, 150—151).—The author employs two platinum wires connected with a battery and an electric bell; the wires are coated with the fat or wax, then immersed together in mercury, which is gradually heated; when the fat melts, the circuit closes, the bell then rings, and the temperature is read.

D. A. L.

**Melting Points of Mixtures of Optical Isomerides.** By M. CENTNERSZWER (*Zeit. physikal. Chem.*, 1899, 29, 715—725).—The melting point curves for various mixtures were first determined in the

case of two indifferent compounds, and found to consist of two portions with a minimum. The curves of two active optical isomerides are completely symmetrical with two minima and a maximum at the melting point of the inactive compound, which may, however, be either higher or lower than that of the active components. The addition of either active component to the inactive compound, or the reverse, causes a depression of the melting point, but apparent exceptions occur in the cases of dimethylic tartrate and tartaric acid. The first of these is probably due to the minima being too near the axis of coordinates, and the second to homogeneous crystallisation (compare Küster, *Abstr.*, 1892, 396). In general, the results are in complete accord with the statements of Roozeboom (*this vol.*, ii, 355). I. M. J.

**Vapour Pressure Measurements.** By ULRICH DÜHRING (*Zeit. physikal. Chem.*, 1899, 29, 730—731).—A reply to observations made by Kahlbaum in his paper on this subject (*Abstr.*, 1898, ii, 556).

L. M. J.

**Direct Determination of Heats of Combination of Halogen Compounds: Aluminium Bromide.** By NICOLAI N. BÉKÉTOFF (*Chem. Centr.*, 1899, i, 1062; from *Bull. Acad. St. Pétersbourg*, [v], 10, 79—81).—The heat of combination of aluminium and bromine to form  $Al_2Br_6$ , has been directly determined, and found to be 41,000 cal. per atom of bromine. Thomsen and Berthelot's indirect determinations gave 40,000 and 42,000 cal. respectively. E. W. W.

**Thermochemical Measurements.** By MARCELLIN P. E. BERTHELOT (*Compt. rend.*, 1899, 129, 320—321).—The results are summarised in the following table:

	Heat of combustion.			Heat of	
	1 gram. cal.	1 mol. at const. v. Cal.	1 mol. at const. p. Cal.	formation from elements. Cal.	dissolu- tion at about 25°. Cal.
Cholic acid .....	7985	3401·7	3406·1	306·35	—
Amygdalin .....	5139·6	2348·7	2349·2	468·5	—
Conicine .....	10027·7	1273·5	1275·5	65·4	+5·1
Ethylenediamine.....	—	—	—	8·8	+7·45
Ethylenediamine hydrate .....	—	—	—	80·6	+4·68
Ethylenediamine dihydrochloride ...	—	—	—	124·5	+6·65

The formation of cholic acid from cholesterol by oxidation would correspond with a considerable development of heat. The hydrolysis of amygdalin is accompanied by very little thermal disturbance.

The heat of neutralisation of conicine by hydrochloric acid is 11·4 Cal. The heat of dissolution of conicine hydrochloride obtained from Kahlbaum was -0·87 Cal., whilst the same compound prepared from Merck's conicine gave -1·49 Cal. Probably they were salts of isomeric conicines. The heat of formation of conicine hydrochloride is lower than that of ammonium chloride, but higher than that of aniline hydrochloride. The difference between the heats of formation of conicine

and piperidine (40.9 Cal.) is much higher than would be the case if they were normal homologues (17 Cal.).

The heat of hydration of ethylenediamine is +2.77 Cal., and does not differ greatly from the heat of combination of liquid ammonia and water, +3.11 Cal. Its heat of neutralisation is +12.4 for the first equivalent and +10.8 for the second. The heat of formation of the solid dihydrochloride from the liquid base and the gaseous acid is +70.9 Cal. In the activity of its basic function, ethylenediamine hydrate is comparable with ammonium and potassium hydroxides. C. H. B.

**Thermochemistry of Salicylaldehyde, Parahydroxybenzaldehyde, and Salicylhydramide.** By MARCEL DELÉPINE and PAUL RIVALS (*Compt. rend.*, 1899, 129, 520—523).—The authors have redetermined the thermochemical constants of salicylic acid and some of its derivatives, there being discrepancies between the recorded results of different observers.

*Salicylic acid.*—Molecular heat of combustion at const. vol. and const. pressure, 728.2 Cal., the mean of this and Stohmann's values being 728.3 Cal. Heat of formation from elements +138.8 Cal.; from solid phenol and carbonic anhydride +7.7 Cal., which differs from Berthelot and Werner's direct determination (+6.3 Cal.).

*Salicylaldehyde.*—Heat of combustion, 1 gram, +6527.4 cal.; molecular heat of combustion, 796.34 Cal. at const. vol., and 796.6 Cal. at const. pressure; heat of formation from elements, +70.5 Cal.; heat of oxidation to salicylic acid, +68.3 Cal.

*Parahydroxybenzaldehyde.*—The corresponding values are 6500.6 cal., 793.07 Cal., 793.3 Cal., +73.8 Cal. and +67.4 Cal.

In both cases, the heat of oxidation approximates to that of benzaldehyde, anisaldehyde, and cinnamaldehyde.

*Salicylhydramide*, contrary to the statements of previous observers, always melts at 167°, by whatever method it may be prepared, and, contrary to the statement of Ettling, is rapidly decomposed by acids and alkalis at the ordinary temperature. Heat of combustion (1 gram), 7305.6 cal.; molecular heat of combustion, 2527.73 Cal. at const. vol., and 2528.9 Cal. at const. pressure; heat of formation from elements, +72.4 Cal., and from ammonia and salicylaldehyde  $2 \times 12.95$  Cal. The action of potassium hydroxide on the hydramide takes place in two stages, the first development of heat, 3.1 Cal., corresponding with the saturation of the third phenolic function of the hydramide. This indicates that two of the phenolic functions have been saturated by the nitrogen, which becomes quinquevalent, and this in its turn explains why salicylhydramide is yellow and not white, like most hydramides.

Parahydroxybenzaldehyde does not yield a corresponding hydramide. C. H. B.

**Heat of Neutralisation and Electrolytic Dissociation.** By WILHELM VAUBEL (*Chem. Zeit.*, 1899, 23, 764—765).—The author attempts to explain the constant value of 137—138  $k$  [ $k=100$  cal.] for the heat of neutralisation of strong bases and acids. His method of calculation of the molecular association (*Abstr.*, 1898, ii, 593) indicates that in liquid water the molecule consists of 6 simple molecules and the heat of association is 726  $k$ . The solution of base and acid and the subse-

quent neutralisation are then represented, thus : (i)  $\text{MOH} + 6(\text{H}_2\text{O}) = \text{M}, \text{H}_2\text{O} + \text{OH}, 5\text{H}_2\text{O}$ ; (ii)  $\text{A}, \text{H} + 6(\text{H}_2\text{O}) = \text{A}, 5\text{H}_2\text{O} + \text{H}, \text{H}_2\text{O}$ ; (iii)  $\text{OH}, 5\text{H}_2\text{O} + \text{H}, \text{H}_2\text{O} = (\text{H}_2\text{O})_6 = \frac{1}{6}(\text{H}_2\text{O})_6$ ; the heat development for this latter equation is calculated to be  $142.4 k$ , a number not far removed from the experimental values. The author considers that the electric charges of the hydroxyl and hydrogen ions must pass over to the metallic and acid ion during neutralisation, and that this explains the higher E.M.F. necessary for the decomposition of the salt. He further attempts to show that his thermal values also explain the value of 0.59 volt which Glaser found for the decomposition potential of the hydroxyl ions (this vol., ii, 79). L. M. J.

**Thermal Effects of the Dilution of certain Salts.** By FRANCIS P. DUNNINGTON and T. HOGGARD (*Amer. Chem. J.*, 1899, 22, 207—211).—The authors give a table showing the thermal effect of adding successive gram-molecules of water to nearly saturated solutions of ammonium acetate, lithium chloride, sodium bromide, magnesium nitrate, and calcium, magnesium and strontium chlorides; in all these cases, heat is developed on dilution, and it appears that by far the greater part of the thermal change occurs during the addition of the first few molecules of water. In the case of solutions of ammonium and sodium nitrates, ammonium, sodium and potassium chlorides, and potassium bromide and iodide, the same is true, but the dilution is endothermic; a solution of calcium nitrate, however, on dilution, at first gives out heat, but subsequently absorbs it. W. A. D.

**Cryoscopic Measurements.** By A. PONSOT (*Bull. Soc. Chim.*, 1899, [iii], 21, 764—765).—A former paper by the author (this vol., ii, 546) requires sundry corrections, which do not, however, invalidate the conclusions arrived at therein. N. L.

**Cryoscopic Depression in, and Latent Heat of Fusion of, Naphthylamine and Diphenylamine.** By JOHN MASON STILLMANN and R. E. SWAIN (*Zeit. physikal. Chem.*, 1899, 29, 705—710).—The molecular cryoscopic depressions for solutions in diphenylamine and in naphthylamine do not agree with those calculated by the van't Hoff expression  $0.0199 T^2/w$ . The authors have therefore redetermined the cryoscopic depressions and the latent heats of fusion, as well as incidentally the specific heats of solid and liquid, in the case of pure specimens of the two compounds, a form of calorimeter designed by Waterman being employed. The cryoscopic determinations agreed completely with those of Eijkman, and the other values were diphenylamine, m. p.  $54.0^\circ$ , latent heat of fusion, 23.97; naphthylamine, m. p.  $50.1^\circ$ , latent heat of fusion, 25.59. The cryoscopic constants calculated from these numbers are 81.2 for naphthylamine and 88.8 for diphenylamine, agreeing well with the experimentally determined values 78 and 88 (*Abstr.*, 1889, 666). L. M. J.

**Method for Vapour Density Determination.** By LUDWIG WILHELM WINKLER (*Chem. Zeit.*, 1899, 23, 627).—The method is similar to that of Dumas; the apparatus consists of a thin-walled glass bulb of about 100 c.c. capacity, drawn out to a long, narrow neck which can be closed by a ground stopper. The bath is a modified

V. Meyer constant temperature bath, and the glass bulb does not come in contact with the boiling liquid. The bulb, full of air, is heated for 10 minutes in the bath, the stopper (slightly greased) inserted, and the whole weighed when cold; the operation is then repeated with the gas or vapour whose density is required. J. J. S.

**Change of Volume at the Transition Point of Boracite.** By WILHELM MEYERHOFFER (*Zeit. physikal. Chem.*, 1899, 29, 661—664).—At a temperature of from  $260^{\circ}$  to  $270^{\circ}$ , boracite undergoes a transition from the rhombic to the regular system, and the author, employing the dilatometric method, shows that this transition occurs at  $266^{\circ}$  and is accompanied by a decrease in volume. L. M. J.

**Application of Molecular Volumes.** By ANATOLE LEDUC (*Ann. Chim. Phys.*, 1899, [vii], 17, 173—196).—The paper contains several tables showing the differences between the specific volumes of isopentane, ether, carbon bisulphide, and water vapours obtained by direct experiment and those calculated by the author from critical constants. The experimental data bearing on the dissociation of chlorine, nitric peroxide, and acetic acid vapour, are also discussed (compare *Abstr.*, 1898, ii, 471, and this vol., ii, 354).

The atomic weight of hydrogen obtained by the author's calculations is 1.0076 ( $O=16$ ) and agrees closely with the value deduced from Sacerdote and Berthelot's experiments (this vol., ii, 404). G. T. M.

**Dissociation of Nitric Peroxide.** By A. POCHETTINO (*Real. Accad. dei Lincei*, 1899, 8, 183—188).—A series of 29 measurements was made of the wave-length of sound in nitric peroxide at temperatures ranging between  $4.2^{\circ}$  and  $150^{\circ}$ , Kundt's formula being employed in calculating the results. The density of the gas at each temperature was taken from the tables of Natanson and of Troost and Deville, intermediate values being obtained by means of Gibbs' formula for the density of a dissociated gas. From the numbers thus found, the corresponding values  $k$  of the ratio of the specific heats have been calculated; the values of  $k$  have also been deduced from the law of mixtures, the gas being taken as a mixture of  $N_2O_4$  and  $NO_2$  in proportions given by its density.  $k$  is found to increase regularly with the temperature from 1.17 to 1.30, these values corresponding respectively with the hexatomic molecule  $N_2O_4$  and the triatomic molecule  $NO_2$ ; the agreement between the two sets of values is satisfactory. T. H. P.

**Theory of Diffusion.** By EMIL BOSE (*Zeit. physikal. Chem.*, 1899, 29, 658—660).—From the equation for the diffusion of a non-electrolyte, that for the diffusion of a completely dissociated compound as deduced by Nernst, and the equilibrium equation  $kc=(A-c)^2$ , the author deduces expressions available for the diffusion of partially dissociated electrolytes, for which, however, no experimental support is offered although they are capable of such verification. L. M. J.

**Diffusion of Ions into Gases.** By JOHN S. TOWNSEND (*Proc. Roy. Soc.*, 1899, 65, 192—196).—A gas which has been ionised by the action of Röntgen rays gradually loses its conductivity if left to itself;

the ions partly recombine and partly give up their charges to the walls of the containing vessel. If a stream of an ionised gas be passed through a metal tube of small bore, the loss of conductivity due to recombination of the ions will be negligible compared with that due to the absorption of the ionic charges by the metal tube. This latter will depend on the diffusion of the ions, and a mathematical discussion shows how the coefficient of diffusion may be calculated from the reduction of conductivity. With the help of the values obtained, it is shown that the ionic charges produced by Röntgen rays in air, oxygen, carbonic anhydride, and hydrogen are all the same and equal to the charge on a hydrogen ion in a liquid electrolyte. The number of molecules in 1 c.c. of a gas is estimated as  $2 \times 10^{-19}$ , and the weight of a molecule of hydrogen is calculated to be  $4.5 \times 10^{-24}$  grams.

J. C. P.

**A Hydrate Theory of Solution.** By FLAVIAN FLAWITZKY (*Chem. Centr.*, 1898, i, 651—653; from *J. Russ. Chem. Soc.*, 29, 565—583).—A mathematical discussion leads the author to the conclusion that the same law applies to electrolytes as to non-electrolytes. Two types of solutions are distinguished: (1) normal solutions, in which the existence of normal hydrates can be demonstrated; (2) abnormal solutions, which give no indication of the formation of normal hydrates. The difference in the two cases depends only on the relative stability of the hydrates.

The extent of hydration in solution is directly proportional to the molecular weight; the same holds for cryohydrates, and the author therefore believes that the latter have an important influence on the properties of aqueous solutions.

J. C. P.

**Laws of Solutions.** By WLADIMIR A. KISTIAKOWSKI (*Chem. Centr.*, 1899, i, 89—91; from *J. Russ. Chem. Soc.*, 1898, 30, 576—585).—Apparatus is described in which osmotic pressure in gases may be observed and determined, the method depending on the fact that many membranes, &c., are permeable to some gases but not to others. Argon is found to diffuse through caoutchouc 100 times as rapidly as carbonic anhydride, and by means of a caoutchouc membrane separating air and ether vapour a rise in pressure of 15 cm. of mercury was observed. The laws of osmotic pressure are calculated from the basis of the law that in a system in equilibrium a small disturbance is not associated with any energy change, hence if a gas be in equilibrium with a solution  $p dv - q dv_1 = 0$ , where  $p$  is the partial pressure of the gas,  $q$  its osmotic pressure, and  $dv$  and  $dv_1$  the respective volumes in the gaseous state and in the solution, and hence, since  $dv/dv_1$  is constant  $qv_1 = RT$ . The author also shows that in the calculation of the cryoscopic depression a term involving the heat of dilution is necessary, the expression obtained being  $T - T_1 = T/Q(RT/1000V_1 + Z)$  where  $Z$  is the heat liberated when 1 gram of the solvent is withdrawn from the quantity of solution which contains 1 gram-molecule of the solute. Comparison with the depression obtained in hydrogen chloride solutions shows that when this correction is applied the calculated values agree well with determinations for cryoscopic depressions as high as  $28.8^\circ$ . L. M. J.



**Solid Solutions and Isomorphous Mixtures of Saturated and Non-saturated Open-chain Compounds. I. and II.** By GIUSEPPE BRUNI and F. GORNI (*Real. Accad. dei Lincei*, 1899, [v], 8, 454—463, and 570—579. Compare Abstr., 1898, ii, 562).—In ethylenic bromide solution, ethylenic chlorobromide has the molecular weight 343—359, the normal value being 143·5, and in the same solvent, ethylenic cyanide gives the values 98—135, the number corresponding with the formula being 80.

Dissolved in dimethylic succinate, dimethylic maleate shows normal, and dimethylic fumarate abnormal, cryoscopic behaviour; in the latter case, the molecular weights found are 797 to 914 instead of 144. As regards crystalline form and configuration, fumaric and succinic acids are closely related, whilst maleic acid has no such similarity with succinic acid.

Using butyric acid as solvent, the cryoscopic behaviour of crotonic acid, is abnormal and that of isocrotonic acid normal. Since crotonic acid melts at a higher temperature than the corresponding saturated acid and further is more stable than the iso-acid, the fumaroid formula must be assigned to it and to isocrotonic acid the corresponding maleoid formula.

In phenylpropionic acid solution, cinnamic acid raises the point of solidification, whilst allocinnamic acid gives the normal depression. Cinnamic acid has therefore a fumaroid molecular configuration, allocinnamic acid being the corresponding maleoid form.

Cryoscopic determinations of the molecular weight of elaidic acid in stearic acid solution give the value 303—315 instead of the normal number 282; also, stearic acid dissolved in elaidic acid has the molecular weight 348—370, whilst the formula corresponds with the number 284. These abnormal values show that stearic acid and elaidic acid form solid solutions, and to the latter must be attributed a fumaroid configuration, the isomeric oleic acid being the corresponding maleoid compound (Garelli and Montanari, Abstr., 1895, ii, 205). These conclusions are borne out by the greater stability towards reagents, and the higher melting point, of elaidic acid.

Muthmann (Abstr., 1898, i, 614) has shown that if the  $\text{CH}_2$ -group of potassium or ammonium methanedisulphonate be replaced by  $\text{NH}$ , the imidosulphonates thus obtained are isomorphous with the corresponding methanedisulphonates. This equivalence of  $\text{CH}_2$  and  $\text{NH}$  does not obtain in the case of some other compounds. Thus diphenylamine shows normal cryoscopic behaviour in diphenylmethane solution. But benzylideneaniline and stilbene both have abnormal molecular weights in azobenzene solution; the isomorphism of stilbene and azobenzene thus indicated is confirmed by crystallographic measurement. Both crystallise in the monoclinic system. For azobenzene,  $[a:b:c = 2:10756:1:1:33123 \text{ and } \beta = 65^\circ 34']$ , whilst for stilbene,  $[a:b:c = 2:17015:1:1:40033 \text{ and } \beta = 65^\circ 54']$ . Hydrazobenzene, benzylaniline, and dibenzyl all show abnormal cryoscopic behaviour in azobenzene. Dibenzyl is also crystallographically completely isomorphous with azobenzene and stilbene, and the last raises the melting point of dibenzyl.

The following conclusions are drawn. 1. The groupings  $-\text{CH}=\text{CH}-$  of a fumaroid compound and  $-\text{CH}_2-\text{CH}_2-$  are isomorphotropic with  $-\text{N}=\text{N}-$ . 2. By substituting  $-\text{N}=\text{CH}-$  for one of the preceding groupings, the compounds retain morphotropic relations and are capable of forming solid solutions. 3. The substitution of  $-\text{NH}-\text{NH}-$  removes all similarity of configuration and hence also the capacity of forming solid solutions. 4. The effect of substituting the grouping  $-\text{CH}_2-\text{NH}-$  is not well defined.

T. H. P.

**Cryoscopic Behaviour of Substances with Constitutions similar to that of the Solvent.** IV. By FELICE GARELLI and F. CALZOLARI (*Real. Accad. dei Lincei*, 1899, [v], 8, 579—590; *Gazzetta*, 29, ii, 258—284. Compare preceding abstract).—When dissolved in thymol, menthol forms solid solutions with it, the molecular weight obtained being 168—177, instead of 156.

The freezing points of mixtures of dibenzyl and stilbene show very considerable differences from the values calculated by means of Küster's law for isomorphous mixtures, the largest difference being  $17.36^\circ$  for a mixture containing 40.66 per cent. of dibenzyl.

In dibenzyl solution, hydrazobenzene gives normal depression of freezing point, whilst azobenzene, benzyldeneaniline, and benzylaniline behave abnormally.

Of the two theoretically possible stilbenes, that known must be regarded as the fumaroid modification.

Dibenzyl, stilbene, azobenzene, and benzyldeneaniline all behave abnormally in benzylaniline solution, as does triphenylamine in triphenylmethane solution.

T. H. P.

**Cryohydric Phenomena in Solutions of Enantiomorphous Isomerides.** By GIUSEPPE BRUNI (*Real. Accad. dei Lincei*, 1899, [v], 8, 332—335).—The method employed by Roozeboom (this vol., ii, 276) for distinguishing between racemic compounds, inactive conglomerates, and pseudo-racemic mixtures by means either of the melting point curve or of the solubility curve of the solid, has a complete analogue in the method suggested by the author, who makes use of the curve of saturation in the case of binary mixtures, and of the cryohydric curve in the case of ternary mixtures. By this means are avoided the disadvantages of Roozeboom's method, which requires relatively large quantities of material, is not applicable to substances decomposing before melting, and, if the solubility curve be employed, involves experimental difficulties.

T. H. P.

**Recognition of Racemic Compounds.** By H. W. BAKHUIS ROOZEBOOM (*Ber.*, 1899, 32, 2172—2177. Compare this vol., ii, 276 and 401; also following abstract).—The author considers that Ladenburg's statements (*Trans.*, 1899, 75, 465; this vol., ii, 551) are less complete than his own (*loc. cit.*), and, as regards some of them, not accurately formulated. He also points out that Ladenburg, in applying to liquid externally compensated compounds the method used in

the case of solids, has paid no attention to the phase rule, and hence his conclusions are invalid; in fact, determinations of solubility are not suitable for determining whether a liquid is a racemic compound or an inactive conglomerate. J. J. S.

**Recognition of Racemic Compounds.** By FREDERIC STANLEY KIPPING and WILLIAM J. POPE (*Ber.*, 1899, 32, 2225—2227. Compare *Trans.*, 1899, 75, 36, and preceding abstract).—It is pointed out that Ladenburg's modified method (*Trans.*, 1899, 75, 465) is essentially different from his original one (*Ber.*, 1894, 27, 3065) and that it is now in accordance with the results described by the authors (*loc. cit.*). The conclusions arrived at by Ladenburg with respect to the racemic nature of liquids such as *i*-pipicoline are invalid, as he has completely neglected the application of the phase rule. J. J. S.

**New Method for the Resolution of Racemic Compounds into the Active Constituents.** By WILHELM MARCKWALD and ALEX. MCKENZIE (*Ber.*, 1899, 32, 2130—2136).—*r*-Mandelic acid has been etherified by the aid of an optically active alcohol, namely, *l*-menthol, and the results indicate that *l*-mandelic acid is not quite so readily etherified as the *d*-acid. The method, however, does not lend itself, at any rate in this case, to the complete resolution of the racemic acid, since after 50 grams of the acid and alcohol had been heated at 155° for 1 hour, only about 0.72 gram of the *l*-acid could be isolated. The menthylic mandelate formed in the reaction, when fractionally hydrolysed, gave first an acid having a slightly positive rotation (but the actual isolation of the *d*-acid was not attempted), and finally an acid with a negative rotation. Although the method is not so efficient as other methods for the resolution of racemic acids, the authors conclude that it may be of practical use for the resolution of racemic alcohols by the aid of an optically active acid. J. J. S.

**Hylotropic-isomeric Forms.** By KARL SCHAUM (*Annalen*, 1899, 308, 18—40. Compare *Abstr.*, 1898, ii, 211 and 372).—The cases of sulphur, tin, hexachloro-*o*-ketodihydrobenzene, nitrosobenzene, and menthol are discussed by the author. M. O. F.

**Gaseous Reactions in Chemical Kinetics. V. Gradual Combination of Oxyhydrogen Gas.** By MAX BODENSTEIN (*Zeit. physikal. Chem.*, 1899, 29, 665—699).—The present paper deals with the non-explosive combination of hydrogen and oxygen when the mixture is passed through porcelain tubes raised to the desired temperature by means of a lead-bath. From the total volume of gas passed through, and the total time, the time during which the gas was exposed to the high temperature is found, and by varying these values various determinations of the velocity constant were made at temperatures of 482°, 509°, 560°, and 572°. The values at each temperature, as calculated for a trimolecular equation, are constant, and equal values were obtained on varying the initial proportions of the two gases; the action hence proceeds according to the equation  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ . The actual values of the constant vary with the form of the tube employed, and the author finds that the ratio of the

constants for two tubes is approximately equal to the ratio of the quotients surface/volume, and hence concludes that the action proceeds almost entirely on the surface of the vessel and not throughout the entire mass, that is, it is a catalytic action. At temperatures which vary from  $660^{\circ}$  to  $700^{\circ}$  for different tubes, the steady union becomes explosive, and as the explosion temperature is approached, the velocity constant, previously in accord with that given by equation  $\log k = A/T + B \log T + c$ , increases enormously above the calculated values. The author considers this to be due to the imperfect conduction of heat, so that the heat generated by the union raises the temperature of the gas above that of the surroundings, and the explosion temperature is hence highest for vessels of greatest comparative surface. The results of the author are not in accord with those previously obtained by Hélier (this vol., ii, 85).

L. M. J.

**Velocity of Explosion of Acetylene.** By MARCELLIN P. E. BERTHELOT and HENRI LE CHATELIER (*Compt. rend.*, 1899, 129, 427—434. Compare Abstr., 1897, ii, 91).—The velocity of explosion of pure (98 per cent.) acetylene was studied at pressures varying from 5 to 36 kilograms per square centimetre, the gas being enclosed in glass tubes 1 metre in length and having an internal diameter of 2—6 millimetres. One end of the glass tube was closed, and the other end connected with an iron vessel in which the explosion was started by firing electrically a detonator of fulminate or chlorate mixture weighing 0.01—0.04 gram. Larger amounts are to be avoided, since they give rise to violent undulatory movements which are not strictly due to the detonation itself. In some cases, the influence of any irregular initial disturbance was obviated by introducing an iron tube, 1.5 metres in length, between the glass tube and the iron vessel. The phenomena observed in the glass tube were registered on a photographic plate which was made to drop in a frame at the moment of firing, so that the image of the flame traversing the tube was recorded in the form of a curve, the inclination of the tangent at any point of the latter being a measure of the velocity at which the explosion is being propagated at the corresponding part of the tube. The results of a number of experiments show that, contrary to what is observed with mixtures of acetylene and oxygen, the velocity of explosion of pure acetylene increases continuously with the propagation of the flame along the tube, which is generally ruptured before a uniform velocity can be attained. The fracture, or rather pulverisation, of the tube takes place, as a rule, when about half its length has been traversed, and is propagated backwards with a velocity comparable with that of the explosion. In the greater number of cases, the curve obtained assumes almost immediately an asymptotic form, indicating that the velocity, after a certain point, increases but slowly until, at the moment of rupture, a large and abrupt increase is noticed. In a considerable number of experiments, however, a more continuous and rapid increase was observed. These different results are independent of the pressure and appear to be connected with differences in the manner in which the explosion is initiated. According to the most uniform and regular determinations, the velocity of explosion increases

with the pressure from 1000 metres per second at 5 kilograms per square centimetre to about 1600 metres at 30 kilograms.

The theoretical signification of the results obtained is finally discussed, and it is pointed out that a fundamental distinction exists between waves, such as those of sound, which are propagated from a single, unrenewed impulse and those occurring in an explosive mixture or an endothermic gas in which a continually increasing amount of energy is set free. The explosive properties of acetylene may be expected to differ from those of combustible gaseous mixtures, since the products of its decomposition, gaseous hydrogen and solid carbon, have very different physical properties. Moreover, in the combustion of hydrogen and gaseous hydrocarbons with oxygen, the carbonic anhydride and water formed, which are partially dissociated at the temperature of explosion, undergo association as the temperature falls and thus modify the violence of the initial shock, whereas acetylene is abruptly resolved into free carbon and hydrogen. N. L.

**Velocity Constants in the Formation of Simple Ethers.** By W. SAGREBIN (*Chem. Centr.*, 1899, i, 1059—1060; from *J. Russ. Chem. Soc.*, 1899, 31, 19—27).—The velocity constants were determined at 100° for the reaction between alcohols and ethereal salts of benzenesulphonic acid with the production of the ether and acid. Excess of the alcohol was employed as a solvent, and on this account the reaction is of the first order. The values for the constant compared with that for methylic alcohol are as follows: methylic alcohol, 100; ethylic alcohol, 48.9; propylic alcohol, 35.2; isobutylic alcohol, 21.4; *i*-isomyllic alcohol, 23.6; octylic alcohol, 16.2; allylic alcohol, 28.1; benzylic alcohol, 14.98. The order, which shows the influence of constitution, is the same as that obtained by Menschutkin for the rate of etherification of alcohols and the velocity of reaction of amines with allylic bromide, although differences occur in the actual numbers, explicable by the use of different solvents (*Abstr.*, 1890, 1366; 1898, i, 119). Values for isopropylic alcohol, 16.1, and phenylmethylcarbinol, 4.5, were also obtained, but with trimethylcarbinol and dimethylethylcarbinol, constant values for the velocity constant were not observed. L. M. J.

**Function of the Medium in Chemical Change.** By JULIUS W. BRÜHL (*Ber.*, 1899, 32, 2326—2331.) [Compare Lowry, *Trans.*, 1899, 75, 215—228].—The velocity of isodynamic change has been studied by means of the refractive and dispersive powers in the case of the enolic and ketonic forms of Claisen's ethylic mesityloxidoxalate (*Abstr.*, 1896, i, 561), dissolved in different media; the refractive powers of the two isomerides are very different, and the dispersive powers differ by 400 per cent.

No isomeric change takes place on dissolving the enolic form, or on diluting the solution, the small changes in the optical constants being due to physical and not to chemical causes. Of the solvents used, chloroform produced the least acceleration, and in this solvent the formation of the ketonic form is hardly perceptible after 2½ months; benzene,  $\alpha$ -bromonaphthalene, and carbon bisulphide act somewhat more rapidly, but the greater part of the enolic form is

unchanged after 3 months; methylic and ethylic alcohol, on the other hand, cause a marked change in a few days, and in 2 or 3 months nearly the whole of the enolic is converted into the ketonic form, the reaction being complete and not proceeding to a state of equilibrium. The isomeric change is regarded as due to the ionic dissociation of the enolic form, followed by a reassociation of the ions in the ketonic form, and it is pointed out that the isomeric change takes place most rapidly in those media which have the greatest dissociating and dielectric power; these media are also usually characterised by great heat of vaporisation, heat of fusion, and specific heat.

T. M. L.

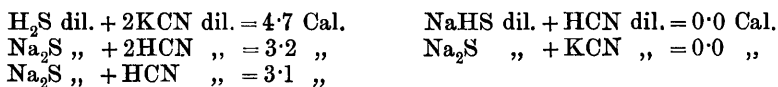
[Dissociation of Molecular Chlorine by Water.] By ALEXANDER A. JAKOWKIN (*Zeit. physikal. Chem.*, 1899, 29, 613—657).—The author has previously shown that in a solution of chlorine in water equilibrium is finally attained when  $\text{Cl}_2 + \text{Aq} \rightleftharpoons \text{Cl}^- + \text{H}^+ + \text{HClO} + \text{Aq}$  (Abstr., 1897, ii, 246), and has now further investigated this equilibrium. As hypochlorous acid is a very weak electrolyte, the conductivity of chlorine solutions is almost entirely due to the hydrogen chloride, and the concentration of the latter can therefore be determined from conductivity experiments. By subtraction of double the quantity of chlorine so found from the total chlorine, the concentration of undissociated molecules is obtained, and it is found that when the concentration is so calculated, the partition ratio of chlorine between carbon tetrachloride and water is constant for all concentrations, so that the quantity of undissociated chlorine in water may be calculated from that in carbon tetrachloride in equilibrium with the solution. The gas is also shown to be present in both solvents in the form of simple molecules. The hydrolysis in water at various concentrations was then determined and the values of the equilibrium constant were found to remain constant when calculated for the trimolecular equation  $k.c = (A - c)^3$ . If chlorine ions be added, the dissociation of molecular chlorine must decrease, and, by addition of chlorides, this was found to be the case, the equilibrium constant for  $kc = (A - c)^2(A - c + b)$  being equal to that previously obtained. In strong solutions, apparent variations occur consequent on the alteration of the partition ratio. Undissociated chlorides should produce no effect, but it was found that mercuric chloride causes a slight increase of dissociation which is explicable by the union of the salt with some hydrogen chloride (Le Blanc and Noyes, Abstr., 1891, 388). The effect of hydrogen ions, which should be equal to that of chlorine ions, was found to be in entire accord with theory, the acids employed being dilute sulphuric, nitric, acetic, and the three chloroacetic acids. Boric acid, which is practically undissociated, has no effect except in strong solutions. Hydrochloric acid yields both hydrogen and chlorine ions and its effect is therefore considerably greater than that of other acids, the dissociation being in this case given by  $kc = (A - c)(A - c + b)^2$ . In solutions of hydrochloric acid, therefore, of moderate strength, the dissociation of the chlorine is very slight; for high concentrations, however, the results are complicated, owing to the formation of the trichloride  $\text{HCl}_3$ . The agreement of all the determinations with those calculated by the tri-

molecular equation is well seen by comparison of the experimental values with the theoretical curves, and conclusively proves the dissociation. The latter may also be calculated entirely from conductivity observations, and the results so obtained agree completely with the former determinations. The equilibrium constant increases with rise of temperature, so that the hydrolysis is accompanied by heat absorption, which decreases from about 7 Cal. at ordinary temperature to zero at from 75° to 95°, and the heat of solution of undissociated chlorine may also be calculated. The results are in accord with the determinations of Thomsen, and with the values for the hydrolysis calculated from the heats of formation of hydrochloric and hypochlorous acids.

L. M. J.

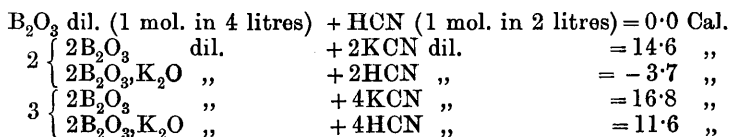
**Equilibrium between Hydrocyanic and other Acids in Combination with Alkalis.** By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1899, [vii], 17, 453—457).—Potassium cyanide is completely decomposed by hydrochloric acid; when solutions containing each of these reagents are mixed at 15°, the heat developed is 10·7 Cal.; the same value is obtained for nitric acid, whilst 10·3 Cal. are developed in the case of acetic acid; these figures coincide with the theoretical values.

When solutions containing phenol (1 mol. in 20 litres) and potassium cyanide (1 mol. in 2 litres) are mixed together, 5·2 Cal. are developed. The hydrocyanic acid appropriates 3/5ths of the base, although its heat of neutralisation in solution is less than one-third that of phenol, but since the heats of formation of solid potassium cyanide and potassium phenoxide from solid generators are (20·2 - *S*) and 12·4 Cal. respectively, where *S* (representing the heat of fusion of solid HCN) is not greater than 4 Cal., it follows that hydrocyanic acid is in reality a stronger acid than phenol. The following data are obtained with hydrogen sulphide (1 mol. in 20 litres):



These results indicate that excess of hydrogen sulphide completely displaces hydrogen cyanide from solutions of its alkali salts.

Analogous conditions of equilibrium exist between carbonic and hydrocyanic acids; those obtaining with the latter compound and boric acid are indicated by the following data:



The alkali is shared between the two acids; in experiment 2, which corresponds with the monobasic borate, the hydrocyanic acid takes 1/6th of the base; in experiment 3 (dibasic borate), it takes 4/9ths.

G. T. M.

**Dissociation of Ammonio-metallic Salts.** By R. JARRY (*Ann. Chim. Phys.*, 1899, [vii], 17, 327—388).—The paper contains descriptions of apparatus employed in preparing ammonio-silver salts and in studying their dissociation.

When a concentrated ammoniacal solution of silver chloride is allowed to evaporate over quicklime, the ammonio-silver chloride,  $2\text{AgCl}\cdot 3\text{NH}_3$ , separates in colourless, birefractive prisms not affected by light; when the solution is placed over anhydrous calcium chloride, ammonia is removed, and the compound,  $\text{CaCl}_2\cdot \text{NH}_3$ , is produced, this has a lower dissociation pressure than the ammonio-silver salt, and accordingly the latter dissociates, yielding crystalline silver chloride. The ammonio-silver chloride,  $\text{AgCl}\cdot 3\text{NH}_3$ , crystallises in long, colourless, birefractive needles when a solution of silver chloride in liquid ammonia is evaporated at  $-40^\circ$  to  $-20^\circ$ ; the substance is not affected by light. Silver chloride is only slightly soluble in liquid ammonia, and a convenient apparatus is described which obviates the use of large quantities of the solvent in preparing the ammonio-silver chloride crystals. Silver iodide, unlike the chloride or iodide (compare Abstr., 1897, ii, 259, and 1898, ii, 515), is extremely soluble in liquid ammonia, and on allowing the solution to evaporate at  $-40^\circ$  to  $-10^\circ$ , white, birefractive, lamellar crystals of the ammonio-silver iodide,  $\text{AgI}\cdot \text{NH}_3$ , are obtained; this substance dissociates at  $4^\circ$  under atmospheric pressure, forming a second ammonio-iodide,  $2\text{AgI}\cdot \text{NH}_3$ . The dissociation pressures of the two compounds are as follows:

				$\text{AgI}\cdot\text{NH}_3$				
$t$	$-23^\circ$	$-13^\circ$	$0^\circ$	$6\cdot 2^\circ$	$10\cdot 5^\circ$	$15^\circ$	$20\cdot 5^\circ$	
$p$	145	80 [1]	585	820	1055	1380	2020 mm.	
				$2\text{AgI}\cdot\text{NH}_3$				
$t$	$0^\circ$	$19^\circ$	$37^\circ$	$39^\circ$	$52\cdot 5^\circ$	$65^\circ$	$80^\circ$	$100^\circ$
$p$	3	12	57	63	155	270	485	1145 mm.

The latter compound is obtained in the crystalline form by the spontaneous evaporation of a solution of silver chloride in concentrated aqueous ammonia; it separates in small, white crystals which become dark violet on exposure to light; during the crystallisation, the pressure of the dissolved ammonia in the liquid surrounding the crystals must be greater than the dissociation pressure of the substance, otherwise the latter dissociates, yielding silver iodide.

Methylammonio-silver bromide,  $\text{AgBr}\cdot \text{NH}_2\text{Me}$ , is quite analogous to the corresponding chloride (compare Abstr., 1897, i, 455), and is prepared in a similar manner. Its dissociation pressures are as follows:

				$\text{AgBr}\cdot \text{NH}_2\text{Me}$		
$t$	$0^\circ$	$19\cdot 5^\circ$		$20\cdot 5^\circ$	$45\cdot 2^\circ$	$55^\circ$
$p$	11	52		58	290	514 mm.

The following table indicates the solubility of silver bromide in 10 c.c. of aqueous methylamine of different concentrations at  $11\cdot 5^\circ$ :

$\text{NH}_2\text{Me}$ . Grams.	$\text{AgBr}$ . Mgrm.	$\text{NH}_2\text{Me}$ . Grams.	$\text{AgBr}$ . Mgrm.	$\text{NH}_2\text{Me}$ . Grams.	$\text{AgBr}$ . Mgrm.	$\text{NH}_2\text{Me}$ . Grams.	$\text{AgBr}$ . Mgrm.
4·844	289	3·562	73	1·797	28	1·317	12
4·311	127	3·258	55	1·513	16	1·101	7



The curve representing these results shows a break corresponding with a solution saturated under the dissociation pressure of  $\text{AgBr}, \text{NH}_2\text{Me}$ .

The methylammonio-silver iodide,  $\text{AgI}, \text{NH}_2\text{Me}$ , obtained like its analogues, forms white, birefractive crystals not affected by light; its dissociation pressures are as follows:

$t$	0°	15°	25.5°	29.5°	34°	38°	40°	45°	47°	51°	56°	60°
$p$	35	142	300	403	550	713	803	1130	1210	1360	1575	1745 mm.

At 39°, under atmospheric pressure, this substance is wholly converted into another methylammonio-iodide,  $2\text{AgI}, \text{NH}_2\text{Me}$ , which gives the following dissociation pressures:

$t$	0°	19°	34°	47.5°	65°
$p$	11	34	60	116	228 mm.

These two compounds are very insoluble in aqueous solutions of methylamine, and on this account the latter iodide could not be obtained crystalline.

The dissociation curve of the compound,  $\text{AgI}, \text{NH}_2\text{Me}$ , is discontinuous at the point corresponding with the temperature 43° and the pressure 1070 mm.; at this temperature, the substance is seen to melt; the lower portion of the curve therefore represents the dissociation of the solid, and the upper portion that of the liquid, ammonio-iodide.

G. T. M.

**Equilibrium in the System, Water-Phenol-Aniline.** By FRANS A. H. SCHREINEMAKERS (*Zeit. physikal. Chem.*, 1899, 29, 577—602).—The equilibrium relations had been previously studied for the system, water-alcohol-succinonitrile (*Abstr.*, 1898, ii, 564), in which two of the pairs form two liquid phases between certain temperature limits. The present system is in this respect similar, but it yields a different form of equilibrium field, and the binodal curves for various temperatures are given, as well as the prismatic representation. The critical mixture temperature of the water-phenol system is 68°, and replacement of phenol by aniline causes a regular increase of this temperature to 167° for the water-aniline system. Curves are also constructed to show the effect of addition of aniline to a mixture of water and phenol in constant ratio, and in this case the critical temperature first rises and then again falls. The addition of salt raises, but that of alcohol lowers, the critical mixture temperature of phenol and water. If one constituent be added to a mixture of the other two, the composition of the homogeneous phase varies for varying ratios of the binary mixture, and curves are given to show the two correlated compositions. The theoretical considerations are postponed.

L. M. J.

**False Equilibrium.** By PIERRE DUHEM (*Zeit. physikal. Chem.*, 1899, 29, 711—714).—The author replies to Bodenstein's criticisms (this vol., ii, 639) of the work of Pelabon, and considers that the observations of the former respecting the limits of temperature of formation and false equilibrium of hydrogen sulphide are incorrect. The discrepancies between the results of Bodenstein and of Pelabon are regarded as due to the fact that the former has overlooked the

absorption of hydrogen sulphide by liquid sulphur, and on this account the use of indefinite quantities of sulphur militates greatly against the value of his researches.

L. M. J.

**Fixed Points of Transformation.** By HENRI LE CHATELIER (*Compt. rend.*, 1899, 129, 497—499).—Reversible transformations, such as fusion, allotropic changes, &c., are usually considered to take place under fixed external conditions, but the author does not consider that this is necessarily an absolute law. The equilibrium conditions in a heterogeneous system are  $\epsilon - T\eta + Pv - M_1m_1 - \dots - M_nm_n = 0$ , where  $\epsilon$ ,  $\eta$ ,  $v$ ,  $m$ ,  $M$ , are respectively the energy, entropy, volume, mass, and potential, this equation holding for each phase. If, however, changes of magnitude of the particles lead to changes in energy, &c., which may be the case if the particles are very small (for example, the vapour tension of small drops of water), then the above expression may be greater or less than zero. In the former case, the system would be stable, as the subdivided parts would reunite; in the second case, the subdivision could proceed spontaneously, ultimately yielding a homogeneous mixture, and the author does not consider there is any *a priori* reason why this should not occur. Crystalline liquids are, perhaps, cases of the progressive fusion of crystals, but experimental realisation of changes of state at variable tensions is probably difficult.

L. M. J.

**"Genesis of Dalton's Atomic Theory."** By GEORG W. A. KAHLBAUM (*Zeit. physikal. Chem.*, 1899, 29, 700—704).—The author replies to certain criticisms of Debus on the German translation, by the author, of the above work of Roscoe and Harden.

L. M. J.

**The Place of the New Constituents of the Atmosphere in the Periodic System.** By JAMES LEWIS HOWE (*Chem. News*, 1899, 80, 74—76).—Helium, neon, and argon are considered to be the first three elements of the eighth group in Mendeléef's table of the periodic system. Neon hence follows fluorine, and is the transitional element between the halogen and sodium, whilst argon is a transitional element between chlorine and potassium. Helium is thus in the same horizontal series as hydrogen, but the corresponding element of the halogen series is unknown. Other similar elements could be placed in this group, inasmuch as it is a group containing triads, for example, iron, cobalt, nickel, &c.; and the elements metargon, krypton, xenon may perhaps be placed in it. The author considers the position of elements with no chemical affinity as transition elements from the negative halogens to the positive alkali metals to be probable and natural, and the dissimilarity in properties of these elements and the others of the group, iron, platinum, &c., does not, in his opinion, militate against these views, as dissimilarity from the type elements occurs in other groups.

L. M. J.

## Inorganic Chemistry.

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**Solidification of Hydrogen.** By JAMES DEWAR (*Compt. rend.*, 1899, 129, 451—454; *Ann. Chim. Phys.*, 1899, [vii], 18, 145—149; *Chem. News.*, 1899, 80, 132—133).—In earlier experiments, liquid hydrogen was allowed to evaporate under 10 mm. pressure, and gave no sign of solidification. Whilst experimenting with some electric resistance thermometers, the wires being immersed in liquid hydrogen, and a small quantity of air entering through leakages and becoming frozen, it was observed that when the pressure was reduced below 60 mm. the whole of the liquid suddenly solidified into a white, froth-like mass like frozen foam. The solid evaporated completely under the low pressure, and melted when the pressure was allowed to rise to 55 mm.; it therefore could not be regarded as frozen air containing liquid hydrogen, and the fact that solidification did not occur in the earlier experiments is attributed to undercooling. This was confirmed by evaporating liquid hydrogen under 30—40 mm. pressure in a special apparatus; it became completely solid, but melted if the pressure was allowed to rise to 55 mm. The sp. gr. of the solid could not be determined, but the maximum sp. gr. of the liquid is 0·086 as compared with 0·07 at its boiling point.

Measurements with constant volume hydrogen thermometers showed that the temperature of the solid under 35 mm. pressure is 16° absolute. The boiling point under 760 mm. pressure is 21° absolute. Calculating from these data, a vapour tension of liquid hydrogen of 55 mm. would correspond with a temperature of 16·7° absolute, hence the melting point of hydrogen must be about 16° or 17° absolute. It may be noted that the critical temperature of hydrogen being 30° to 32° absolute, the melting point is about half the critical temperature. The melting point of nitrogen is also about half its critical temperature. The lowest temperature that can be obtained by evaporation of solid hydrogen under low pressure is 14—15° absolute.

C. H. B.

**Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination.** By JAMES DEWAR (*Proc. Roy. Soc.*, 1899, 64, 231—238).—By an extrapolation of the vapour pressure curves of oxygen and nitrogen down to the temperature of boiling hydrogen, the vapour pressure of air at that temperature may be estimated as less than one-millionth of an atmosphere. Vacuum tubes of ordinary shape, suited for the spectroscopic examination of gases, had attached to them a temporary tube, which was immersed for over a minute in liquid hydrogen; the solidification of the air in the interior produced a very high vacuum, as was proved by the extreme difficulty of passing a spark through the tubes.

The process brings about a concentration in the vacuum tubes of the more volatile constituents of the air, and spectroscopic examination of a number of tubes prepared in the above way revealed the presence of neon and helium in a volume of air less than 50 c.c. A number of

tubes which had no electrodes showed a carbonic oxide spectrum, due to impurities coming from the glass. Only some tubes showed the hydrogen spectrum, so that the question of the presence of free hydrogen in the air requires further investigation. J. C. P.

**Solubility of Bromine in Water.** By LUDWIG WILHELM WINKLER (*Chem. Zeit.*, 1899, 23, 687).—Pure bromine and water were shaken for an hour at a constant temperature, a portion of the clear solution was then removed by a capillary pipette and added to a concentrated solution of potassium iodide, the liberated iodine being estimated by the aid of sodium thiosulphate.

The mean results obtained were

Temp.	0°	10·34°	19·96°	30·17°	40·03°	49·85°
Parts of water dissolve } 1 part of bromine ... }	24	26·74	27·94	29·10	29·02	28·39

Much less bromine is soluble in ice cold water in the presence of bromine hydrate.

Temp.	0°	5·12°
Parts of water dissolve 1 part of bromine	42·39	26·26

The solubility of bromine vapour in water has also been estimated. Bromine water was shaken in a partially filled vessel, the amount of bromine vapour evolved, and also the amount of bromine left in solution were then determined, and, after calculating the pressure of the bromine vapour, its absorption coefficient was calculated.

Temp.	Pressure.	Absorption coefficient.
0°	56—13	60·53
9·94	89—16	35·22
20·46	138—9	20·87
30·38	179—12	13·65
40·31	229—26	9·22
50·25	274—53	6·50
60·04	314—46	4·84
69·98	154—54	3·82
80·22	396—74	2·94

The absorption coefficient obeys the law previously enunciated (*Abstr.*, 1892, 556). Since only so much liquid bromine is dissolved in water as corresponds with the absorption coefficient of bromine vapour and the tension of liquid bromine, it is merely necessary to determine the first two data for a given temperature and then the tension ( $p$ ) of liquid bromine for that temperature may be calculated by means of the equation  $p = b \cdot 760 / \beta \cdot v \cdot 0\cdot0071426$  where  $b$  = weight of liquid bromine dissolved by 1 gram of water,  $\beta$  = absorption coefficient of bromine vapour,  $v$  = specific volume of water at the given temperature, and  $0\cdot0071426$  gram is the weight of 1 c.c. of bromine vapour at 0° and 760 mm.

It follows that liquid bromine, as such, is not soluble in water, and that only the vapour dissolves. J. J. S.

**Electrolytic Method of preparing Alkali Chlorates, Bromates, and Iodates.** By ERICH MÜLLER (*Chem. Centr.*, 1899, i, 1061; from *Zeit. Elektrochem.*, 5, 469—473).—The conversion of

potassium hypochlorite into chlorate is accelerated by the addition of potassium chromate, and the current yield is increased from 32.8 to 69.6 per cent. or more. Similarly, alkali bromides and iodides are almost quantitatively oxidised into bromates and iodates respectively in the presence of potassium chromate. Platinum is the most suitable metal for the anode; the use of graphite causing impurities in the salts, and platinum, iron, nickel, or copper may be used as cathodes, but not lead or zinc. In order to avoid the formation of perchlorates, the temperature of the chloride solution should not sink below  $25^{\circ}$  nor rise above  $50^{\circ}$ , but perbromates and periodates are not formed from bromides and iodides respectively, even when the solutions are well cooled. The current density may vary within wide limits. Manganese salts have no influence on the formation of chlorates, &c.

E. W. W.

**Iodic and Periodic Acids.** By ARTHUR ROSENHEIM and OTTO LIEBKNECHT (*Annalen*, 1899, 308, 40—67).—The authors' experiments lead them to the following conclusions. (1.) Free iodic acid is dibasic, having the composition  $H_2I_2O_6$ . (2.) The hydrogen iodates have the composition  $RHI_2O_6$ . (3.) The complex iodomolybdates (compare Chrétien, *Abstr.*, 1896, ii, 651) are acid salts of the composition  $RIO_3MoO_3$ , analogous to the hydrogen iodates. (4.) When hydrogen iodates or complex iodates are neutralised, the anion is split, and normal iodates (salts of a hypothetical, monobasic iodic acid) are formed. (5.) Periodic acid is pentabasic. (6.) Powerful bases convert periodic acid into stable, monometallic salts, normal salts of a monobasic, meta-periodic acid.

*Ammonio-silver iodate*,  $AgIO_3 \cdot 2NH_3$ , prepared by allowing a solution of silver iodate in concentrated ammonia to evaporate spontaneously over solid potash in a bell-jar, crystallises in long, highly lustrous needles, and becomes greyish-violet when exposed to daylight.

Disilver hydrogen periodate,  $Ag_2H_3IO_6$ , first described by Magnus and Ammermüller (*Ann. Phys. Chem.*, 1833, [i], 28, 514), is prepared by suspending the sodium salt,  $Na_2H_3IO_6$ , in water, adding just enough nitric acid to dissolve it, and treating the solution with neutral silver nitrate at  $20^{\circ}$ . When the operation is carried out at  $100^{\circ}$ , the black salt,  $Ag_3IO_5$ , is produced, but if the disilver periodate is first isolated and then treated with boiling water, the pale yellow colour changes to reddish-brown, and finally black, whilst the liquid becomes acid; by constantly replacing the water until this no longer shows an acid reaction, the salt,  $Ag_5IO_6$ , is obtained as a black, crystalline powder, and this compound is also produced when disilver hydrogen periodate is treated with ammonia. A boiling solution of the disilver periodate in dilute nitric acid dissolves freshly precipitated silver oxide, forming the black salt,  $Ag_3IO_5$ .

The following silver periodates are known at the present time:  $AgIO_4$ ,  $Ag_2H_3IO_6$  (and its anhydrides,  $Ag_2HIO_5$  and  $Ag_4I_2O_9$ ),  $Ag_3IO_5$ , and  $Ag_5IO_6$ ; Lautsch's tetrabasic salt,  $(Ag_2O)_4I_2O_7$ , is not an individual substance.

*Pentasodium hexatungstoperiodate*,  $5Na_2O \cdot I_2O_7 \cdot 12WO_3 + 16H_2O$ , prepared by boiling a solution of hydrogen disodium periodate with

sodium carbonate ( $1\frac{1}{2}$  mols.) and tungstic acid in slight excess, is the tungsten analogue of Blomstrand's molybdo-salt (Abstr., 1892, ii, 122); it crystallises in microscopic needles, and the aqueous solution gives rise to the corresponding *potassium* salt, with  $8\text{H}_2\text{O}$ , *strontium* salt, with  $28\text{H}_2\text{O}$ , and *barium* salt, with  $12\text{H}_2\text{O}$ .

*Trisodium monotungstoperiodate*,  $3\text{Na}_2\text{O}, \text{I}_2\text{O}_7, 2\text{WO}_3 + 4\text{H}_2\text{O}$ , prepared by adding the disodium periodate (15 grams) in small quantities to a boiling solution of sodium paratungstate (20 grams), forms a white, amorphous mass. The *diammonium sodium* salt,  $2(\text{NH}_4)_2\text{O}, \text{Na}_2\text{O}, \text{I}_2\text{O}_7, 2\text{WO}_3 + 16\text{H}_2\text{O}$ , obtained when ammonia is added to a concentrated solution of sodium hexatungstoperiodate until the precipitate at first formed no longer disappears on stirring, is a crystalline substance.

M. O. F.

**Action of Hydrogen Chloride on Sulphates, Selenates, Tellurates, and Phosphates.** By RAYMOND W. TUNNELL and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 929—932).—Although selenic and telluric acids are readily expelled from their salts by the action of hydrogen chloride, the method cannot be employed for the separation of sulphates from selenates or tellurates, as a certain amount of sulphuric acid is also replaced, but even at a dull red heat the whole of the sulphuric acid is not removed (compare Heusgen, *Ber.*, 1876, 9, 1671). At the ordinary temperature, a reaction takes place, the sulphate increasing in weight, probably owing to the formation of a double salt, such as  $\text{K}_2\text{SO}_4, \text{HCl}$ . The expulsion of the sulphuric acid takes place more readily in the presence of a selenate or tellurate, and the authors consider it a case of mass action.

Selenic or telluric acid may be completely removed from a mixture of phosphate with selenate or tellurate without the loss of any phosphoric acid.

J. J. S.

**Character of the Impurity found in Nitrogen Gas derived from Urea.** By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1898, 64, 95—100).—Nitrogen prepared from carbamide by the action of sodium hypochlorite or hypobromite contains an impurity heavier than nitrogen, the excess amounting to 1—2 per cent. of the weight of pure nitrogen (compare *Phil. Trans.*, A, 1895, 188). When the generating vessel and its charge of hypochlorite were heated previous to the introduction of urea, the weight of impurity was increased. The gas evolved was passed over cold copper turnings, solid caustic potash, and phosphoric anhydride, and only traces of carbonic anhydride or oxygen could be found in the collected gas. With the idea that the impurity was nitrous oxide, the author determined the refractivity of the gas by a method of which details are given, and found that the proportion of impurity indicated in this way was nearly the same as that deduced from the weight. The view that the impurity is nitrous oxide agrees with the observation that it is much more soluble in water than nitrogen. Explosion of the gas with hydrogen gave a contraction rather in excess of the nitrous oxide supposed to be present. It is probable that nitrous oxide is formed by the action of hypobromite on carbamide, as well as in the preparation of nitrogen from chlorine and ammonia.

J. C. P.

**Densities of 'Atmospheric Nitrogen,' Pure Nitrogen, and Argon.** By WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1899, 64, 181—183).—The density of 'atmospheric nitrogen,' calculated from the densities of the constituents taken in the proportion in which they occur, agrees well with the value found by experiment, whether the figures of Leduc and Schlesing or those of Lord Rayleigh and Kellas are taken as the basis of calculation. J. C. P.

**Free Hydrazine.** By CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1899, 18, 297—298. Compare Abstr., 1897, ii, 22).—A preliminary communication relating to the action of sodium, phosphorus, phosgene, sulphurous and carbonic anhydrides, and nitrous oxide on free hydrazine. G. T. M.

**Manufacture of Nitrite.** By A. DARBON (*Chem. Zeit.*, 1899, 23, 173—174).—The author describes the method for the manufacture of sodium nitrite by the action of metallic lead on fused sodium nitrate. It is essential that the lead shall be as free as possible from other metals, especially antimony. After fusion, the mass is poured into water, exactly neutralised with nitric or sulphuric acid, in order to precipitate any lead oxide in solution, filtered, and evaporated. Pure nitrite has a neutral, and not, as usually stated, an alkaline reaction. The best method for estimating the nitrite is by the aid of standard potassium permanganate in the presence of dilute sulphuric acid; in this estimation, only a few c.c. of the acid should be added until the titration is nearly completed, when a larger quantity may be added without any loss of nitrous acid. The pink colour should remain permanent for 15 minutes. J. J. S.

**Thioxyarsenic Acids.** By LEROY W. MCCAY (*Ber.*, 1899, 32, 2471—2476. Compare Abstr., 1898, ii, 139).—Arsenates cannot be detected by magnesia mixture in the solutions obtained by dissolving arsenic pentasulphide in caustic alkalis or ammonia. The reaction is somewhat complicated, the chief products being thioarsenates and monothioxyarsenates; these salts are always accompanied by small quantities of dithioxyarsenates. The solution of pentasulphide in caustic soda, on digestion with strontium chloride, yields a precipitate consisting of strontium monothioxyarsenate and strontium sodium monothioxyarsenate. *Sodium monothioxyarsenate*,  $\text{Na}_3\text{AsSO}_3 + 12\text{H}_2\text{O}$ , is obtained in long needles by boiling this mixture with sodium carbonate, filtering, and adding alcohol to the filtrate.

Barium dithioxyarsenate is precipitated by adding barium chloride to the filtrate from the strontium monothioxyarsenates; on boiling with sodium carbonate, it yields *sodium dithioxyarsenate*,  $\text{Na}_3\text{AsS}_2\text{O}_2 + 10\text{H}_2\text{O}$ , which separates from solution on the addition of alcohol.

Thioarsenates and monothioxyarsenates are also obtained by dissolving arsenic pentasulphide in calcium, strontium, and barium hydroxides.

When hydrogen sulphide is passed into a 1 per cent. solution of arsenic acid, a mixture of arsenic tri- and penta-sulphides and sulphur is precipitated, whilst monothioxyarsenic acid remains in solution; the latter is freed from unchanged arsenic acid by the addition of magnesia; the solution, after filtration, contains magnesium mono-

thioxyarsenate; this is converted successively into the potassium, barium, and sodium salts, and by this method 6 grams of crystallised sodium monothioxyarsenate are obtained from 10 grams of arsenic acid. When hydrogen sulphide is passed into a solution of sodium arsenate acidified with mineral acids, a small quantity of dithioxy-arsenic acid is produced.

G. T. M.

**Products of Combustion of Boiler Fuel.** By WILHELM THÖRNER (*Chem. Zeit.*, 1899, 23, 331—333).—When coal containing sulphur or pyrites is employed as fuel, sulphuric acid, in addition to sulphurous anhydride, is present in the products of combustion. The whole of this acid does not make its escape; part is deposited on the boiler walls, &c., and it is essential that these should be cleaned regularly. The corroding action of the acid is greater when moisture is present. The formation of the acid may be largely diminished, if not completely avoided, by mixing the coal with lime or by using briquettes made of an intimate mixture of coal with a little lime.

J. J. S.

**Action of Chlorine on a Mixture of Silicon, Silica, and Alumina.** By ÉMILE VIGOUROUX (*Compt. rend.*, 1899, 129, 334—335).—Silicon tetrachloride is readily obtained by the action of chlorine at about a red heat on the mixture of silicon, silica, and alumina obtained by reducing silica with aluminium, and treating the product first with hydrochloric acid and afterwards with aqua regia. The proportion of silicon in this product depends on the relative proportions of silica and aluminium, and on the care taken to cool the reduced mass rapidly and out of contact with air; a mixture of 2 parts of silica and 1 part of aluminium gives good results.

C. H. B.

**Preparation, and some of the Properties, of Pure Argon.** By WILLIAM RAMSAY and MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1899, 64, 183—192).—‘Atmospheric nitrogen’ was passed twice over heated magnesium and red-hot copper oxide, the process yielding a gas rich in argon. This gas was then passed (1) through a tube containing a mixture of magnesium powder and lime, heated to a dull red heat in a combustion furnace, (2) over red-hot copper oxide. The whole of the crude argon thus obtained was liquefied in a bulb surrounded by liquid air boiling under a low pressure. When the colourless, mobile, liquid argon is distilled, the first portion to boil off is rich in neon and contains helium, whilst the least volatile portion is metargon. The middle portion is argon, and by a repetition of the process pure argon is obtained.

The density of the gas so purified is 19.957, a value not differing greatly from that previously found, namely, 19.94. The refractivity of pure argon is 0.9665, whilst that of the crude gas was found to be 0.961. Neon and helium have both a low refractivity, and the removal of these gases accounts for the greater refractivity of pure argon. Even at the temperature of boiling oxygen, argon shows no polymerisation, for the ratio  $pv/T$  has practically the same value at that as at higher temperatures.

J. C. P.



**Basic and Ammoniacal Metallic Halogen Salts.** By EUGÈNE TASSILLY (*Ann. Chim. Phys.*, 1899, [vii], 17, 38—125).—The results of work already published (compare Abstr., 1894, ii, 92; 1895, ii, 45, 304, 342, and 500; 1896, ii, 350, 360, and 465; 1897, ii, 451; and 1898, ii, 117).  
G. T. M.

**Metallic Sulphides.** By A. MOURLOT (*Ann. Chim. Phys.*, 1899, [vii], 17, 510—574).—An account of work already published (compare Abstr., 1896, ii, 25, 304, 603; 1897, ii, 372; 1898, ii, 376; this vol., ii, 27 and 97).  
G. T. M.

**Metallic Thiophosphates.** By LUCIEN FERRAND (*Ann. Chim. Phys.*, 1899, [vii], 17, 388—432).—An account of work already published (compare Abstr., 1895, ii, 389; 1896, ii, 418 and 473).  
G. T. M.

**Action of Sodammonium and Potassammonium on Tellurium and on Sulphur.** By C. HUGOT (*Compt. rend.*, 1899, 129, 388—390).—The following compounds have been prepared by the action of sodammonium and potassammonium on tellurium and on sulphur, the method of preparation being the same as that used for obtaining the corresponding selenium compounds (this vol., ii, 650).

With excess of alkali metal, the monotellurides  $\text{Na}_2\text{Te}$ , and  $\text{K}_2\text{Te}$ , and the monosulphides,  $\text{Na}_2\text{S}$ , and  $\text{K}_2\text{S}$ , are obtained as white, amorphous substances, soluble in water, insoluble in liquefied ammonia; they do not absorb ammonia gas. With excess of tellurium or sulphur, the polytellurides or polysulphides  $\text{Na}_2\text{Te}_3$ ,  $\text{K}_2\text{Te}_3$ ,  $\text{Na}_2\text{S}_5$ ,  $\text{K}_2\text{S}_5$  are formed as crystalline compounds which are soluble in water and in liquefied ammonia and absorb ammonia gas. The tellurium used in the preparation of the above compounds was obtained from commercial tellurium, and was purified according to the methods of Metzner and Ditte (Abstr., 1898, ii, 572).  
H. R. LE S.

**Dehydration of Sodium Phosphate Crystals.** By T. C. WHITLOCK and C. E. BARFIELD (*Amer. Chem. J.*, 1899, 22, 214—215).—The water of crystallisation of disodium hydrogen phosphate is removed by heating for 1 hour at  $180^\circ$ , whilst the water of constitution begins to be lost at  $230^\circ$ , and is completely removed in 1 hour at  $300^\circ$ .  
W. A. D.

**Persulphates of Rubidium, Cæsium, and Thallium.** By ARNOTT R. FOSTER and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 934—936).—*Cæsium* and *rubidium persulphates*,  $\text{Cs}_2\text{S}_2\text{O}_8$  and  $\text{Rb}_2\text{S}_2\text{O}_8$ , are obtained as white precipitates when solutions consisting of two-thirds of sulphuric acid of sp. gr. 1.35 and one-third of a saturated solution of the metallic sulphate are electrolysed in a Nernst "divided cell," surrounded by a freezing mixture. 100 parts of water dissolve 3.32—3.49 parts of rubidium persulphate at  $22.5^\circ$ , and 8.71—8.98 parts of cæsium persulphate at  $23^\circ$ .

A white precipitate was also obtained when thallium sulphate solution was electrolysed in a similar manner, but it could not be analysed on account of its instability.  
J. J. S.

**New Explosive and Detonating Materials.** By UGO ALVISI (*Gazzetta*, 1899, 29, ii, 64—81. Compare this vol., ii, 414).—From the results of a large number of tests of explosives and detonators, it is seen that the addition of ammonium perchlorate to a mercury fulminate detonator gives a greater effect with a dynamite only when the latter also contains ammonium perchlorate, and in this case the best detonating mixture consists of equal parts of ammonium perchlorate and mercury fulminate. For dynamite without perchlorate, the greatest effect is obtained with a detonator containing 17—20 per cent. of the perchlorate and 80—83 per cent. of the fulminate.

T. H. P.

**Ammonio-silver Nitrate.** By MARCELLIN BERTHELOT and MARCEL DELÉPINE (*Compt. rend.*, 1899, 129, 326—330).—The reaction  $\text{AgNO}_3 \text{ diss.} + 2\text{NH}_3 \text{ diss.} = \text{AgNO}_3 \cdot 2\text{NH}_3 \text{ diss.}$  develops +13.35 Cal. and the addition of either ammonia or silver nitrate produces no appreciable thermal disturbance, which shows that the compound is not dissociated in solution. The action of nitric acid on the ammoniacal silver nitrate solution develops +12.25 Cal., and this gives for the heat of combination +13.15 Cal. The author considers that silver oxide is first liberated and then converted into ammonio-silver oxide,  $(\text{NH}_3\text{Ag})_2\text{O}$ , which immediately acts on the ammonium of the ammonium nitrate, forming a complex base,  $\text{NH}_3(\text{NH}_3\text{Ag})$ , which exists in the ammonio-silver salts already known. The corresponding oxide in the solid state is identical with fulminating silver.

The dissolution of silver oxide in dilute ammonia develops +10.45 Cal., which is the heat of formation of the dissolved oxide, and is confirmed by indirect methods. Its heat of neutralisation by dilute nitric acid is +13.62 Cal., and therefore the energy of its basic function is comparable with that of potassium and sodium hydroxides. Ammonio-silver nitrate is readily obtained in crystals, as described by previous observers, and its heat of dissolution at  $-15^\circ$  is  $-8.96$  Cal. (4 litres) and  $-8.58$  Cal. (2 litres). Its heat of formation from its elements is +78.45 Cal., and from solid silver nitrate and gaseous ammonia, +34 Cal. Its resolution into gaseous water, silver, and nitrogen develops +87.15 Cal., which explains its explosive properties.

C. H. B.

**Solubility of Lime in Water and Saccharine Liquids.** By JULIUS WEISBERG (*Bull. Soc. Chim.*, 1899, [iii], 21, 773—776).—Determinations of the solubility of lime in water at  $15^\circ$  and at  $20^\circ$  gave results in close agreement with those of Herzfeld. The results of a number of experiments on the solubility of lime in sugar solutions of different strengths at  $15^\circ$  and at  $16$ — $17^\circ$  are given in tabular form and compared with those obtained by Berthelot, Péligot, Petit, and Schatten. Péligot's tables, although most generally used, are considered to be the least accurate, and the solubilities given by previous experimenters are in each case lower than the values obtained by the author. The solubility increases with the amount of sugar present, but the weight of lime dissolved per 100 grams of sugar is greater in weak than in strong sugar solution. Anhydrous calcium oxide is more soluble in sugar solutions than calcium hydroxide, a

result previously obtained by Herzfeld, Loiseau, and by the author, and now again confirmed. N. L.

**Calcium Carbide as a Reducing Agent in Analysis in the Dry Way.** By N. TARUGI (*Gazzetta*, 1899, 29 i, 509—512).—When cupric oxide is heated to a bright red heat (1408°) with five times its weight of calcium carbide, it is completely reduced to metallic copper. By carefully washing with water the mixture of excess of carbide and alloy formed, metallic leaves containing 5—8 per cent. of calcium are obtained; this alloy is unstable and renders water alkaline and turbid. If the washing is continued until the water effects no further change, the percentage of calcium in the alloy is reduced to 1.27—1.5, the substance thus obtained having a sp. gr. 8.329 and remaining unchanged in the air. Salts of copper act similarly to the oxide.

In salts of lead, calcium carbide effects reduction at about 400°, the alloy formed containing about 8 per cent. of calcium; this substance is more readily decomposed by water than the copper compound, and when freshly prepared has a lustrous surface which in the air rapidly gives place to a whitish efflorescence. With lead chromate, besides the alloy of lead and calcium, free chromium is also obtained. All salts of gold, silver, platinum, tin, bismuth, antimony, cadmium, zinc, nickel, and cobalt, on heating with calcium carbide, give calcium alloys readily decomposable by water. Mercury and arsenic salts deposit free mercury and arsenic.

The author recommends the use of calcium carbide in analysis in place of potassium cyanide or formate or the action of the reducing flame. T. H. P.

**Electro-deposition of Brass.** By T. J. BAKER and T. J. BAKER, junr. (*Chem. News*, 1899, 80, 37).—Quantitative electrolytic experiments were made with solutions of copper and zinc cyanides, alone and mixed, the hydrogen evolved being measured and the metal deposited weighed, both from these solutions and from a copper sulphate cell in series with the cyanide solution. The electrochemical equivalent of copper which is deposited from its cyanide solution, whether alone or with zinc, as brass, is always that of the metal in its cuprous state. D. A. L.

**Precipitation of Copper by Zinc.** By JOHN C. SHENGLE and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1899, 21, 932—933).—Although the precipitation of copper by zinc is recommended as a method for the quantitative estimation of copper and gives good results, experiments made by the authors prove conclusively that small amounts of zinc (1—3 per cent.) are always present in the precipitated copper and that the good results are due largely to a balancing of errors. Similarly, silver and copper deposited by the aid of cadmium always contains small quantities of the latter metal. J. J. S.

**Action of Hydrogen Phosphide on Copper Oxide, Hydroxide, and Carbonate.** By E. RUBÉNOVITCH (*Compt. rend.*, 1899, 129, 336—338).—Cupric oxide, prepared by heating the nitrate, is readily

attacked by hydrogen phosphide, at first slowly, and afterwards more rapidly, with considerable development of heat, copper phosphide,  $P_2Cu_5$ , phosphoric acid, and water being formed. Cupric hydroxide is attacked by hydrogen phosphide with great energy, and the proportion of phosphoric acid formed varies considerably, but if the reaction is moderated, it tends to proceed in the same manner as with the oxide.

The basic carbonate,  $2[CuCO_3, Cu(OH)_2] + H_2O$ , is attacked by hydrogen phosphide with considerable development of heat, the reaction being  $5PH_3 + 5[CuCO_3, Cu(OH)_2] = 2P_2Cu_5 + H_3PO_4 + 5CO_2 + 11H_2O$ .

The phosphide  $P_2Cu_5$  is obtained by passing a mixture of hydrogen phosphide and carbonic anhydride over cupric carbonate, and the phosphide  $PCu_3$  is obtained by treating cuprous oxide in the same way.

C. H. B.

**Cupric Hypophosphite and its Decomposition by Precipitated Palladium.** By RODOLPHE ENGEL (*Compt. rend.*, 1899, 129, 518—520).—Cupric hypophosphite is obtained by mixing cupric sulphate and barium hypophosphite solutions and adding alcohol. It forms a brilliant, white precipitate of the composition  $Cu(H_2PO_2)_2$ , and is somewhat stable both in the solid state and in solution. The solid explodes suddenly at about  $90^\circ$ ; a dilute solution can be boiled without decomposing. Precipitated palladium decomposes cupric hypophosphite solutions in accordance with the following equation:  $Cu(H_2PO_2)_2 + 2H_2O = Cu + 2H_3PO_3 + H_2$ , and copper hydride is not formed. If, however, an aqueous solution of the salt is boiled, brown cuprous hydride is first precipitated and rapidly splits up into hydrogen and copper. In the first phase of the reaction, hypophosphorous acid is formed, but is slowly oxidised by the copper at about  $100^\circ$ , whereas with palladium this oxidation takes place at the ordinary temperature.

Hypophosphorous acid and palladium completely reduce bismuth and antimony salts at the ordinary temperature, but in the case of lead and stannous salts the precipitation of the metal interferes with the activity of the palladium.

C. H. B.

**Mercury Derivatives of Nitrogen Compounds.** By LEONE PESCI (*Zeit. anorg. Chem.*, 1899, 21, 361—376).—The author points out that the evidence brought forward by Hofmann and Marburg (this vol., i, 486) in support of the formulæ  $NH_2 \cdot HgCl$  and  $Hg(NH_3)_2Cl_2$  for the infusible and fusible white precipitates obtained from mercuric chloride and ammonia in the presence of a large proportion of ammonium chloride, is unsatisfactory for the following reasons. The decomposition of these salts by a boiling 20 per cent. solution of potassium hydroxide, whereby all the nitrogen is eliminated in the form of ammonia, is no evidence as to their constitution, for mercuriammonium chloride, when treated in this manner, also parts with all its nitrogen. If, however, the infusible precipitate is treated with reagents which decompose ammonium salts but do not decompose mercuriammonium chloride, such as a 2 per cent. solution of potassium hydroxide or a solution of sodium carbonate, one-half only of the nitrogen is eliminated in the form of ammonia, and the

theoretical quantity of mercuriammonium chloride is obtained. This reaction is in accordance with the formula  $\text{Hg}_2\text{NCl}, \text{NH}_4\text{Cl}$ . The fusible precipitate, when treated in the same manner, yields three-fourths of its nitrogen in the form of ammonia, together with the quantity of mercuriammonium chloride theoretically required for the formula  $\text{Hg}_2\text{NCl}, 3\text{NH}_4\text{Cl}$ .

The author maintains that the mercuriammonium salts are all represented by the type  $\text{Hg}_2\text{NX}$ , and are derived from the hydroxide  $\text{Hg}_2\text{N}\cdot\text{OH}$ , which readily yields complex compounds when treated with ammonium salts. Millon's base is therefore represented by the formula  $\text{Hg}_2\text{N}\cdot\text{OH}, 2\text{H}_2\text{O}$ . The salts obtained from this compound by Hofmann and Marburg by the action of hydrochloric, nitric, and hydrobromic acids were probably not pure. E. C. R.

**Action of Potassium Iodide on Mercurous Iodide.** By MAURICE FRANÇOIS (*J. Pharm.*, 1899, [vi], 10, 16—18. Compare *Abstr.*, 1896, i, 22; ii, 248, 301; and 1897, ii 492).—A solution of potassium iodide decomposes mercurous iodide into mercuric iodide and mercury. If mercury is allowed to remain in contact with a solution of potassium iodide saturated with mercuric iodide, the reverse action takes place, mercurous iodide being formed. In both cases, the action is limited, and for a temperature of  $20^\circ$  equilibrium is established between the reacting substances, when the liquid contains 11.9 per cent. of mercuric iodide. H. R. LE S.

**Photographic Researches on Phosphorescent Spectra: Victorium, a new Element associated with Yttrium.** By SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1899, 65, 237—243).—The method of separating victoria from earths of the cerium group and from yttria is described in detail. Long-continued fractionations (*a*) by fusion and partial decomposition of the nitrates, (*b*) by crystallisation of the oxalates, and (*c*) by precipitation with potassium sulphate, were had recourse to in succession, and the course of the fractionation is shown by a diagram.

Victoria is an earth of a pale brown colour, easily soluble in acids, and less basic than yttria. Assuming the oxide to have the formula  $\text{Vc}_2\text{O}_3$ , the atomic weight is about 117. The best material for phosphorescing in a vacuum tube is, not the earth itself, but the anhydrous sulphate; the photographed phosphorescent spectrum contains a pair of strong lines at about  $\lambda 3120$  and  $3117$ , and other fainter lines at  $3219$ ,  $3064$ ,  $3060$ . J. C. P.

**Porcelain from Egypt.** By HENRI LE CHATELIER (*Compt. rend.*, 1899, 129, 387—388).—An analysis of a sample of Egyptian porcelain which came from Saggarah (Memphis) gave the following results:  $\text{Na}_2\text{O}$ , 5.8;  $\text{CuO}$ , 1.7;  $\text{CaO}$ , 2.1;  $\text{Al}_2\text{O}_3$ , 1.4;  $\text{Fe}_2\text{O}_3$ , 0.4;  $\text{SiO}_2$ , 88.6 per cent. The above composition is totally different from that of Chinese porcelain, and as the sample was undoubtedly of Egyptian origin, the author believes that the ancient Egyptians did manufacture real porcelain. A porcelain identical to the above may be produced by fusing a mixture of 40 parts blue glass, 50 parts fine sand, and 5 parts white clay. H. R. LE S.

**Egyptian Pottery.** By HENRI LE CHATELIER (*Compt. rend.*, 1899, 129, 477—480).—The statuettes found in Egyptian tombs were regarded by Salvétat as carved out of a natural grit, the glaze being a sodium calcium silicate containing copper. The author finds, however, that statuettes from several different localities consist mainly of fine grains of quartzose sand, mixed with a small quantity of clay, which serves as a cement. The glaze is a mixture of grains of sand with a glass of the composition  $4 \text{ SiO}_2$ ,  $0.33 \text{ CuO}$ ,  $0.67 \text{ Na}_2\text{O}$ . C. H. B.

**Chemical Equilibrium between Manganous Hydroxide and Ammonium Salts.** By W. HERZ (*Zeit. anorg. Chem.*, 1899, 21, 243—249).—The statement that manganous salts are not precipitated by ammonia in the presence of ammonium salts is not quite correct. A mixture of equal volumes of normal solutions of manganous sulphate and ammonium chloride in an atmosphere of hydrogen gives a cloudiness on the addition of about one and a-half times the quantity of  $N/10$  ammonia solution; the further addition of ammonia does not appreciably increase the precipitate, which is deposited after the mixture has remained for some hours. The author has examined the reaction which takes place when manganous hydroxide is treated with solutions of ammonium chloride, nitrate and sulphate in an atmosphere of hydrogen, as expressed by the equation  $\text{Mn}(\text{OH})_2 + 2\text{NH}_4\text{Cl} \rightleftharpoons \text{MnCl}_2 + 2\text{HN}_4\text{OH}$ . The reaction does not follow the laws of mass reaction, and the results do not agree with those obtained by Lovén for magnesium salts (*Abstr.*, 1896, ii, 413). The abnormal results are probably due to the combination of the manganese and ammonia to form complex cations. E. C. R.

**Decomposition of Monomanganous Phosphate by Water at  $0^\circ$  and at  $100^\circ$ .** By GEORGES VIARD (*Compt. rend.*, 1899, 129, 412—414. Compare this vol., ii, 26).—Monomanganous phosphate,  $\text{MnH}_4(\text{PO}_4)_2 + 2\text{H}_2\text{O}$ , dissolves in 100 times its weight of water at  $0^\circ$  without appreciable decomposition, but as the weight ( $P$ ) of the salt which is added to the water increases, more and more of the dibasic phosphate,  $\text{Mn}_2\text{H}_2(\text{PO}_4)_2 + 6\text{H}_2\text{O}$ , is precipitated, and the ratio ( $R$ ) of the total phosphoric acid remaining in solution to the combined phosphoric acid increases from 1.06 to 1.19 as  $P$  increases from 10 to 100. When heated with water at  $100^\circ$ , the precipitate consists solely of Erlenmeyer and Heinrich's ditrimanganous phosphate,  $\text{Mn}_2\text{H}_2(\text{PO}_4)_2 + \text{Mn}_3(\text{PO}_4)_2 + 4\text{H}_2\text{O}$ , but in this case the ratio  $R$  increases rapidly until a maximum value of 1.88 is reached, when  $P = 20$ , and then slowly decreases until, when  $P = 150$ , it becomes sensibly constant and equal to about 1.5. N. L.

**Destructive Action of Water containing Free Carbonic Anhydride on Iron.** By OTTO KRÖHNKE (*Chem. Centr.*, 1899, i, 907—908; from *Gesundheit*, 14, 72—75).—The water of St. Johann a/Saar, which is of only  $2^\circ$  hardness and contains 38 milligrams of free carbonic anhydride per litre with only traces of carbonates, was found to attack iron conduit pipes, forming a rust of the following composition:  $\text{Fe}_2\text{O}_3$ , 72.76 per cent.;  $\text{Fe}$ , 13.95;  $\text{H}_2\text{O}$ , 8.69;  $\text{CO}_2$ , 2.9;  $\text{CaSO}_4$ , 0.78;  $\text{Cl}$ , traces; soluble in hydrochloric acid, 0.5. This action, which

must be due to the free carbonic anhydride present, is decreased by the addition of calcium salts for the presence of a certain quantity of calcium hydrogen carbonate causes the formation of a layer of calcium carbonate which protects the iron from further corrosion. Neither the rust nor the water after its passage through the pipes contained sulphides or iron sulphate, hence Rosenblum's theory of the process according to which free hydrogen is assumed to reduce the calcium sulphate to sulphide, which is then decomposed by the carbonic anhydride with liberation of hydrogen sulphide, is not confirmed.

E. W. W.

**Action of Sulphurous Acid on Metallic Sulphates, especially on Ferric Sulphate.** By UBALDO ANTONY and E. MANASSE (*Gazzetta*, 1899, 29, i, 483—488).—Manganese, nickel, cobalt, and ferrous sulphates are not affected when sulphurous anhydride is passed through their aqueous solutions. In the case of ferric sulphate, however, the action is similar to that on ruthenium sulphate (Antony and Lucchesi, this vol., ii, 299), ferrous dithionate being formed. Using a 2 per cent. solution of ferric sulphate at 0°, equilibrium is reached when 80 per cent. of the total sulphate has been converted into dithionate; this percentage diminishes as the temperature rises until, at 95°, no conversion takes place.

T. H. P.

**A new Hydrate of Ferrous Potassium Sulphate, and the Relative Solubilities of the various Hydrates of this Salt.** By FRIEDRICH W. KÜSTER and A. THIEL (*Zeit. anorg. Chem.*, 1899, 21, 116—121).—When molecular quantities of ferrous sulphate and potassium sulphate in mixed solution are allowed to crystallise between 35° and 85°, a pale green salt of the composition  $K_2SO_4 \cdot FeSO_4 + 4H_2O$  separates. The colourless hydrate,  $K_2SO_4 \cdot FeSO_4 + 2H_2O$ , crystallises as the stable form above 90°, but if allowed to cool in contact with the mother liquor, is transformed into the tetrahydrated salt.

The relative stability of the three hydrates, with six, four, and two molecules of water, is shown by a comparison of their solubilities at various temperatures. Nearly saturated solutions of each were shaken up with a further quantity of the same hydrate, and the amount in solution was determined at intervals by titration of a portion with permanganate. At temperatures where the hydrate under examination is stable, the volume of permanganate used reaches a maximum and remains permanently constant.

If the hydrate is unstable at the temperature of the experiment, the volume of permanganate used reaches a maximum, and then gradually alters until the value is reached corresponding with the stable hydrate. The temperature of transformation for the pair of hydrates with six and four molecules of water is about 30°, for the pair with four and two molecules about 87°, and for the pair with six and two molecules about 54°.

J. C. P.

**Atomic Weight of Cobalt.** By THEODOR WILLIAM RICHARDS and GREGORY PAUL BAXTER (*Zeit. anorg. Chem.*, 1899, 21, 250—272. Compare Abstr., 1898, ii, 377).—The authors have determined the weight of cobalt obtained from a known weight of cobalt bromide by

reducing it in a current of hydrogen. The apparatus employed and the method of conducting the analysis are the same as those previously employed for the determination of the atomic weight of nickel (this vol., ii, 488). The cobalt bromide (similarly to the nickel bromide) contains a small quantity of sodium bromide, and this is estimated by extracting the reduced cobalt with water and precipitating with silver. The metallic cobalt resembles nickel in being slightly attacked and dissolved by water, but the solution is quickly oxidised in the air and all the cobalt precipitated as cobalt hydroxide, so that, after separating this by filtration, the weight of the impurities can be obtained by evaporating the solution to dryness and weighing. The authors' experiments prove that the cobalt bromide is completely reduced, and that the impurities are entirely extracted from the reduced metal by water. The complete analysis of the cobalt bromide gave 26.923 per cent. Co, 72.981 per cent. Br combined with the cobalt, 0.070 per cent. Br in the impurities, and 0.033 per cent. Na = 100.007. The mean of twelve determinations gave as the atomic weight of cobalt, Co = 58.995, the extreme values being 59.021 and 58.955 [ $O = 16$ ]. The results do not agree so closely as those obtained for nickel, and the authors are engaged in a further determination of the atomic weight by a different method.

E. C. R.

**Chromylamide.** By JULIUS OHLY (*Chem. News*, 1899, 80, 134).—By treatment with dry ammonia, potassium chlorochromate yields potassium amidochromate,  $KO \cdot CrO_2 \cdot NH_3$ , and this, when dissolved in water, mixed with concentrated ammonia, covered with a layer of ether and treated with chlorine, yields a light brown solution which deposits yellowish-brown, dull, metallic leaflets of *chromylamide*,  $CrO_3(NH_3)_2$ . It evolves ammonia when rubbed with soda-lime, is soluble in water, and its solution gives amide reactions with silver nitrate and lead acetate.

D. A. L.

**Tungsten Chlorobromides.** By ED. DEFACQZ (*Compt. rend.*, 1899, 129, 515—518).—When liquid hydrogen bromide is allowed to act on tungsten hexachloride at the ordinary temperature, it yields the chlorobromide  $WCl_3Br_3$ , whilst at 60—70° the compound  $WCl_6 \cdot 3WBr_6$  is obtained. The latter forms small, olive-green crystals which melt at 232° and dissolve in many organic solvents. It is very unstable, alters rapidly when exposed to air, is immediately decomposed by water, and by steam at 200°, and is readily attacked by hydrogen, oxygen, chlorine, sulphur, phosphorus, halogen hydracids, hydrogen sulphide, nitric and sulphuric acids, alkalis, oxidising mixtures, and potassium hydrogen sulphate. The compound  $WCl_3Br_3$  is very similar in appearance and properties.

C. H. B.

**Chloriodides [and Bromides] of Tin.** By C. LENORMAND (*J. Pharm.*, 1899, [vi], 10, 114—117. Compare this vol., ii, 33).—When the compound  $SnCl_2I_2$  is fractionally distilled in air, the liquid which passes over at 280° solidifies to a mass of orange-red crystals of the composition  $SnClI_3$ . When the fraction 126—180° is redistilled in a vacuum, the distillate consists of stannic chloride, and the residue of the chloriodide,  $SnCl_3I$  or  $SnCl_2I_2$ , according to the proportion of



liquid which has passed over. When the compound  $\text{SnCl}_2\text{I}_2$  is distilled in a vacuum, the distillate consists of stannic chloride, and the residue of stannic iodide.

Iodine is without action on stannous bromide at the ordinary temperature, but at  $100^\circ$  an energetic action takes place, and the compound  $\text{SnBr}_2\text{I}_2$  is formed. This crystallises in hexagonal plates, melts at  $50^\circ$ , boils at  $225^\circ$ , and has a sp. gr. 3.631 at  $15^\circ$ . It is only slightly soluble in cold, but readily in warm, water, and at  $80^\circ$  its aqueous solution is decomposed into hydrated oxide of tin, and hydrogen bromide and iodide. When distilled in air, the bromiodide  $\text{SnBr}_3\text{I}$  passes over between  $230^\circ$  and  $250^\circ$ , and  $\text{SnBr}_2\text{I}_2$  between  $250^\circ$  and  $275^\circ$ , the residue consisting of the compound  $\text{SnBrI}_3$ . Distilled in a vacuum, it boils at  $130^\circ$  and partially distils, the temperature gradually rises to  $180^\circ$ , where it remains stationary, and the compound  $\text{SnBr}_3\text{I}$  passes over whilst the residue in the flask has the composition  $\text{SnBrI}_3$ .

H. R. LE S.

**Electro-deposition of Vanadium.** By SHERARD COWPER-COLES (*Chem. News*, 1899, 79, 147—148).—Vanadium can be obtained as a brilliant, metallic deposit by a current of 18 to 20 ampères per square foot and an E.M.F. at the terminals of the electrolysing cell of 1.88, using a solution of the following composition and working at  $82.5^\circ$ : 1.75 parts of vanadic anhydride dissolved in 2 parts of caustic soda and 160 parts of water and then treated with 32 parts of hydrochloric acid.

D. A. L.

**Influence of Oxidising Substances on the Solubility of Gold in Alkali Cyanides.** By EMILIO NOELTING and G. FOREL (*Chem. Centr.*, 1899, i, 823—824; from *Bull. Soc. ind. Mulhouse*, 1899, 28—43).—The solubility of gold in solutions of alkali cyanides is considerably increased by the addition of  $\alpha$ -nitroso- $\beta$ -naphthol,  $\alpha$ -nitroso- $\alpha$ -naphthol,  $\beta$ -nitroso- $\alpha$ -naphthol, the nitroso-salt,

$\text{C}_{10}\text{H}_4\text{O}(\text{SO}_3\text{Na})_2\text{:NOH}$  [ $\text{NOH} : \text{O} : (\text{SO}_3\text{Na})_2 = 1 : 2 : 3 : 6$ ], nitrosophenol, dinitrosoresorcinol, and nitrobenzene, and to a less extent by orthonitrophenol, potassium ferricyanide, ammonium persulphate, quinonedichlorimide, picric acid, sodium isopurpurate, and oil of turpentine. The solubility is not affected by the presence of potassium nitrite or ammonium vanadate, but it is decreased by ether, chloranil, quinone,  $\beta$ -naphthaquinone, phenanthraquinone, and magenta, whilst methylene-blue and Ponceau-2R render gold insoluble.

The coefficients of solubility under given conditions of temperature, time, concentration of the solution, quantities of cyanide employed, &c., are given in tables in the original paper.

E. W. W.

**Electro-deposition of Palladium.** By SHERARD COWPER-COLES (*Chem. News*, 1899, 79, 280).—For the deposition of palladium in a bright form, a 0.62 per cent. solution of palladium ammonium chloride, in a 1 per cent. solution of the same salt [ $\frac{1}{2}$  of ammonium chloride] is employed. The solution is maintained at a temperature of about  $24^\circ$ , the current used per square foot being about 0.12 ampère, and the E.M.F. at the terminals of the bath 4 to 5 volts.

D. A. L.

Ruthenium and its Compounds. II. Potassium Ruthenichloride. By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1899, 29, ii, 82—84. Compare this vol., ii, 558).—Potassium ruthenichloride is obtained in a pure state by the following method. A mixture of 6 parts of potassium hydroxide and 1 part of powdered ruthenium is heated to fusion in a silver basin, and potassium chlorate added in small quantities with stirring until the ruthenium is completely dissolved. After heating at a high temperature until all evolution of gas ceases, the excess of chlorate being then decomposed, the cold mass, which is of an orange-red colour, is dissolved in cold water, and very dilute hydrochloric acid added until the solution gives a decided acid reaction. When allowed to evaporate at the ordinary temperature in a vacuum over quicklime, this liquid gradually deposits the ruthenichloride which is purified by repeated crystallisation. Thus prepared, potassium ruthenichloride,  $K_2RuCl_6$ , is a reddish-brown powder composed of very minute crystals; in cold water, it is very slightly soluble, but in presence of potassium chloride quite insoluble, and in hot water it dissolves readily with partial decomposition.

T. H. P.

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## Mineralogical Chemistry.

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**Albertite-like Asphalt from Indian Territory, U.S.A.** By JOSEPH A. TAFF (*Amer. J. Sci.*, 1899, [iv], 8, 219—224).—The material described occurs as strings and veins, up to 25 feet thick, in greenish shales at several localities in the McAlister Quadrangle, Choctaw Nation, Indian Territory. It is jet-black, and in the upper parts of the veins is very friable with an uneven fracture, whilst at greater depths it has a smooth, conchoidal fracture. When heated, it softens and decomposes without fusing, but the distillation products differ from those of coal. It is soluble to the extent of over 35 per cent. in carbon bisulphide, and is almost insoluble in turpentine; it thus differs from coal, which is insoluble in carbon bisulphide, and from albertite, which is largely soluble in turpentine. Analyses, I by W. F. Hillebrand, and II by W. C. Day, were made on different samples of material.

	C.	H.	N.	S.	O.	Ash.	H <sub>2</sub> O.	Fixed C.	Volatile combustible material.	Sp. gr.
I.	—	—	—	1.47	—	1.45	0.25	55.97	42.33	—
II.	86.57	7.26	1.48	1.38	2.00	1.31	—	—	—	1.175

L. J. S.

**Composition of Natural Thio-salts.** By CONSTANTIN GUILLEMAIN (*Inaug. Diss.*, Breslau, 1898, 47 pp. Compare *Jahrb. f. Min.*, 1899, ii, Ref. 190—195).—The results are given of 37 analyses made

on various mineral thio-salts; in most cases, only massive material was used, and in only one instance was the material determined crystallographically. In the method of analysis, the material was first decomposed by nitric acid.

*Emplectite*, acicular crystals in quartz from Tannenbaum, Saxony; after deducting more than 50 per cent. of quartz, the mean (I) of two analyses agrees with  $\text{Cu}_2\text{S}, \text{Bi}_2\text{S}_3$ .

*Aikinite* (patrinite), acicular crystals in quartz from Beresovsk, Urals; after deducting about 75 per cent. of quartz, the mean (II) of two analyses agrees with  $\text{PbCuBiS}_3$ .

		Bi.	Cu.	Pb.	S.	Total.
Emplectite...	I.	61.95	18.80	—	19.16	99.91
Aikinite .....	II.	36.22	11.01	35.58	16.58	99.39

*Zinckenite*, from Wolfsberg, Harz; anal. III, on a drusy mass of crystals; IV, on massive material. Formula,  $\text{PbS}, \text{Sb}_2\text{S}_3$ .

*Dufrenoyite*, from the Binnenthal, Switzerland; V, on crystal fragments from the surface; VI, the underlying material. Formula,  $2\text{PbS}, \text{As}_2\text{S}_3$ .

*Jamesonite*, VII, feather ore (a soft, felty mass of fine fibres and needles) from Wolfsberg, Harz; VIII, feather ore from Bräunsdorf, Saxony; IX, minute crystals in cavities of massive material (anal. X) from Arnsberg, Westphalia [compare heteromorphite, this vol., ii, 431]; XI, massive, from Wolfsberg; XII, feather ore from Wolfsberg. Analyses VII—X give the formula  $2\text{PbS}, \text{Sb}_2\text{S}_3$ ; the other two, and previous analyses not agreeing with this formula, are assumed to contain admixed stibnite.

*Boulangerite*, XIII, compact, finely granular material from Oberlahr on the Rhine; XIV, ditto, from Betzdorf on the Sieg; XV, ditto, from San Antonio, California; XVI and XVII, Websky's "epiboulangerite," containing admixed galena, from Altenberg, Silesia. Of these, XIII and XV give the formula  $3\text{PbS}, \text{Sb}_2\text{S}_3$ ; previous analyses not agreeing with this formula are supposed to contain admixed stibnite, jamesonite, pyrites, &c. (compare Abstr., 1898, ii, 29).

*Geocronite*, XVIII, massive, from Sala, Sweden; mean of two analyses giving the formula  $5\text{PbS}, (\text{Sb}, \text{As})_2\text{S}_3$ .

*Bournonite*, XIX, mean of two analyses on crystal fragments from Liskeard, Cornwall; XX, mean of two analyses on material from Wolfsberg, Harz; Formula,  $\text{PbCuSbS}_3$ .

*Jordanite*, anal. XXI, bright crystals with twin lamellæ, from the Binnenthal, Switzerland; sp. gr. 5.48; formula,  $4\text{PbS}, \text{As}_2\text{S}_3$ . XXII is the mean of three analyses made on dull, black material from the Binnenthal; it is much fractured, and is coated with a white crust of arsenious acid; it is probably altered jordanite; formula,  $\text{Pb}_6\text{As}_2\text{S}_{10}$ .

*Enargite*, XXIII, mean of four analyses on massive material intergrown with pyrites, from San Juan Co., Colorado; XXIV and XXV, each the mean of two analyses on massive material intergrown with pyrites, from Morococha, Peru; formula,  $\text{Cu}_7\text{As}_2\text{S}_9$ .

		As.	Sb.	Pb.	Cu.	Fe.	S.	Total.
Zinckenite .....	III.	—	42·43	33·52	0·80	—	23·01	99·76
	IV.	—	42·15	34·33	0·70	0·06	22·63	99·87
Dufrenoy'site .....	V.	21·01	—	57·38	—	—	21·94	100·33
	VI.	20·04	—	56·73	—	—	21·18	97·95
Jamesonite.....	VII.	—	30·04	50·32	—	—	19·69	100·05
	VIII.	—	29·03	51·71	—	—	19·23	99·97
	IX.	—	29·49	50·57	—	—	19·91	99·97
	X.	—	29·51	50·36	—	—	20·15	100·02
	XI.	—	30·73	49·49	—	—	19·68	99·90
	XII.	—	31·23	48·25	—	—	20·32	99·80
	XIII.	—	22·69	58·58	—	—	18·76	100·03
Boulangerite .....	XIV.	—	23·82	57·23	—	—	18·23	99·28
	XV.	—	22·76	59·01	—	—	18·22	99·99
	XVI.	—	16·26	63·73	—	2·42	17·53	99·94
	XVII.	—	14·63	66·06	—	2·34	16·83	99·86
Geocronite .....	XVIII.	4·54	9·27	68·90	—	—	17·13	99·84
Bournonite .....	XIX.	—	25·38	41·42	12·99	—	19·92	99·71
	XX.	—	24·30	42·36	13·28	—	19·91	99·85
Jordanite ..	XXI.	12·46	—	68·67	—	—	18·81	99·94
	XXII.	8·97	—	72·44	—	—	18·58	99·99
Enargite .....	XXIII.	15·27	1·59	—	47·80	1·31	33·84	99·81
	XXIV.	16·53	—	—	46·25	2·19	34·89	99·86
	XXV.	15·34	1·26	—	46·92	1·51	34·49	99·52

L. J. S.

**Cerium in Bismutite from Argentina.** By GUILLERMO BODENBENDER (*Zeit. prakt. Geol.*, 1899, 322—323).—Bismutite occurs in a vein in gneiss at La Toma, Sierra de San Luis; it is grey and compact, or forms a granular, crystalline aggregate with fibrous fracture and silky lustre. Embedded in it are quartz, mica, and grains of columbite, and it is sometimes coated with bismuth ochre. Analysis gave:

Bi <sub>2</sub> O <sub>3</sub> .	CO <sub>2</sub> .	H <sub>2</sub> O.	CaO.	MnO.	FeO.	Ce <sub>2</sub> O <sub>3</sub> .	Total.
80·7	8·7	1·9	6·7	0·8	0·3	0·54	99·6

L. J. S.

**Formation of Corundum in Magmas.** By JULIUS H. PRATT (*Amer. J. Sci.*, 1899, [iv], 8, 227—231).—The author has previously noted the occurrence of chromite, corundum and spinel in the peridotites (dunite, &c.) of North Carolina (Abstr., 1898, ii, 603; this vol., ii, 494). Morozewicz's recent experiments (this vol., ii, 762) were made on magmas containing alkalis and alkaline earths, but his earlier experiments (Abstr., 1895, ii, 275) showed that alumina readily dissolves in a magma having the composition of a basic magnesian rock, and that it separates out again as corundum and spinel. The conditions for the separation of corundum from such magmas are summarised as follows.

In a magnesium silicate magma containing no excess of magnesia, all the alumina separates out as corundum; but when there is an excess of magnesia, this unites with a portion of the alumina to form spinel, and the remainder of the alumina separates as corundum. When chromic oxide is present, any small amounts of alumina and excess of magnesia in the magma may enter into the composition of the chromite (mitchellite, this vol., ii, 495). In a peridotite magma

containing, besides alumina, oxides of the alkalis and alkaline earths, a portion of the alumina is used to unite with these oxides and silica to form felspar.

L. J. S.

**Emery from Virginia.** By W. W. MILLER, jun. (*Amer. Chem. J.*, 1899, 22, 212—213).—Analysis of emery from near Whittle's, Pittsylvania Co., gave

$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Na}_2\text{O}$ .	Total.
56.74	15.50	20.77	0.68	1.86	3.95	99.50

It forms a black, crystalline mass, magnetic; polar; sp. gr. 4.205; H on edges 8; infusible, and does not lose in weight on ignition. Omitting the silica, titanite oxide, and soda, the composition corresponds with a mixture of 22.48 per cent. of magnetite, 33.34 per cent. of hercynite, and 37.16 per cent. of corundum. The erosive power is not sufficient to give it value as emery.

W. A. D.

**The so-called Valleriite.** By JAKOB PETRÉN (*Jahrb. f. Min.*, 1899, ii, Ref., 17—18; from *Geol. För. Förh.*, 1898, 20, 183—192).—Valleriite was the name given by Blomstrand in 1870 to a mineral substance from Nya Kopparberg, Sweden, which, according to his analyses, had the composition  $2\text{CuS}, \text{Fe}_2\text{S}_3 + 2\text{MgO}, \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O}$ . A chemical and microscopical examination of the material shows it to be a mixture of covellite, pyrrhotite and spinel, together with hydro-talcite, chalybite, and limonite as secondary products. The covellite ( $\text{CuS}$ ) separated from the mixture has the composition, Cu, 62.35; S, 34.83; Fe, 2.37 = 99.55 per cent. The separated spinel has the following composition:

$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MgO}$ .	Total.
67.75	2.88	0.86	27.04	98.53

L. J. S.

**Formation of Oceanic Salt Deposits, particularly of the Stassfurt Beds. XII. Hydrate of Magnesium Sulphate,  $\text{MgSO}_4 + \frac{5}{4}\text{H}_2\text{O}$ .** By JACOBUS H. VAN'T HOFF and H. M. DAWSON (*Chem. Centr.*, 1899, i, 1137—1138; from *Sitzungsber. Akad. Wiss. Berlin*, 1899, 340—343).—When a solution of magnesium sulphate containing magnesium chloride is concentrated at 65°, the dihydrate,  $\text{MgSO}_4 + 2\text{H}_2\text{O}$ , separates in cauliflower-like bundles of slender needles which soon change to more transparent and crystalline masses of the composition  $\text{MgSO}_4 + \frac{5}{4}\text{H}_2\text{O}$ . Experiments with the dilatometer showed that the same hydrate,  $\text{MgSO}_4 + \frac{5}{4}\text{H}_2\text{O}$ , may be obtained by adding a crystal of it to a solution of magnesium sulphate containing magnesium chloride which has deposited all its tetrahydrate at 25°. This hydrate also separates spontaneously when the solution is very slowly concentrated.

E. W. W.

**Minerals of Sarrabus, Sardinia.** By G. B. TRAVERSO (*Jahrb. f. Min.*, 1899, ii, Ref., 218—221; from *Sarrabus e suoi minerali*, Alba, Piedmont, 1898).—Descriptions are given of the numerous mineral species occurring in the mineral veins of Sarrabus; analyses are given of the following:

Embolite contains 61.1 AgCl and 29.4 AgBr. Native silver gave

the results under I; also traces of lead and zinc. Massive argentite gave II.

Ullmannite gave analysis III, by Mascazzini; also impurities 9.736 per cent.

	Ag.	Cu.	As.	Sb.	S.	Hg.	Ni.	Co.	AgCl.
I.	91.07	0.26	0.12	0.07	0.28	0.03	trace	—	0.87
II.	83.0	1.2	—	0.9	12.0	trace	0.4		—
III.	0.1	—	0.78	52.51	13.37	—	24.0	—	—

Partial analyses are also given of impure arsenic and antimony compounds of nickel and cobalt.  
L. J. S.

**Occurrence of Iodine in Cuprite and in Malachite.** By WILHELM AUTENRIETH (*Chem. Zeit.*, 1899, 23, 626. Compare Abstr., 1897, ii, 561).—A number of specimens of cuprite and malachite from New South Wales have been found to contain small quantities of iodine, the amount varying from 0.006—0.15 per cent. It is thought probable that the iodine is present in cuprite in the form of cuprous iodide (marshite) and in malachite as a basic cupric iodide,  $\text{OH} \cdot \text{CuI}$ .

J. J. S.

**Occurrence of Iodine in Cuprite and in Malachite.** By CARL OCHSENIUS (*Chem. Zeit.*, 1899, 23, 669. Compare preceding abstract).—The author draws attention to the conversion of sulphide ores into halogenised ores in the Andes of both North and South America. In Chili, chlorides occur in the upper, iodides in the lower, and bromides in the intermediate layers.

J. J. S.

**Iodine in Copper Ores from New South Wales.** By ARTHUR DIESELDORFF (*Zeit. prakt. Geol.*, 1899, 321—322).—Copper ores—cuprite, malachite and chrysocolla—from several localities, Cobar, Broken Hill, &c.—were found to contain small amounts of iodine, from 0.01 to 0.14 per cent., together with a little silver. The occurrence of iodyrite ( $\text{AgI}$ ) and marshite ( $\text{CuI}$ ) at Broken Hill suggests that the iodine is present as iodides of silver and copper.

L. J. S.

**Formation of Manganosite and Periclase** By HJALMAR SJÖGREN (*Jahrb. f. Min.*, 1899, ii, Ref., 15—16; from *Geol. För. Förh.*, 1898, 20, 25—32. Compare Abstr., 1897, ii, 324).—Manganosite ( $\text{MnO}$ ) and periclase ( $\text{MgO}$ ) occur under the same conditions as original constituents in dolomitic limestone at Långban and at Nordmark, Sweden. The methods successful in the artificial production of these minerals are, on account of the high temperature employed, not in accordance with those which must have occurred in their natural formation. Analysis by R. Mauzelius of the pure dolomitic limestone, which is the matrix of periclase, gave

Insol.	$\text{SiO}_2$ .	$\text{Fe}_2\text{O}_3$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{CO}_2$ .	Total.
1.26	0.18	0.08	6.38	30.62	16.21	[45.27]	100.00.

The dolomitic matrix of manganosite contains more manganese and less magnesium than shown in this analysis.

Since alkali carbonates precipitate both hydroxides and carbonates from cold dilute solutions of magnesium and manganese salts, the

hydroxides could have been deposited at the same time as the dolomite ; these hydroxides are now partly represented by original brucite,  $\text{Mg}(\text{OH})_2$ , and pyrochroite,  $\text{Mn}(\text{OH})_2$ , and partly by the periclase and manganosite, the dehydration probably taking place at the same time that the limestone became crystalline. Secondary brucite and pyrochroite, derived by the subsequent alteration of the periclase and manganosite respectively, also occur in the dolomitic limestone.

L. J. S.

**Smithsonite from Arkansas.** By W. W. MILLER, jun. (*Amer. Chem. J.*, 1899, **22**, 218—219).—Smithsonite, from the "Morning Star" mine, Searcy Co., Arkansas, gave on analysis,

ZnO.	CdO.	CuO.	FeO.	CO <sub>2</sub> .	SiO <sub>2</sub> .	Total.
63·67	1·06	0·21	0·07	34·69	0·52	100·22

It occurs in botryoidal form and encloses zinc blende in layers 6—8 mm. thick. It is greyish-white in colour with a pearly lustre, translucent, H=5, sp. gr. 4·179.

W. A. D.

**Manganese Silico-carbonates from Hautes-Pyrénées.** By HERMANN LIENAU (*Chem. Zeit.*, 1899, **23**, 418—419).—*Viellaurite* is the name given to a massive, dark-grey mineral with granular structure from the Coustou mine near Vielle-Aure in Hautes-Pyrénées. On exposure to the air, it becomes black. The powder is almost white, and is completely decomposed by acids with separation of gelatinous silica. The mean results of the analyses are given under I ; formula,  $5\text{MnCO}_3, 2\text{Mn}_2\text{SiO}_4$ .

SiO <sub>2</sub> .	CO <sub>2</sub> .	MnO.	FeO.	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	S.	H <sub>2</sub> O.	Total.	Sp. gr.
I. 11·93	21·09	63·01	1·56	1·06	0·77	—	0·55	—	99·97	3·7
II. 19·24	15·00	48·65	0·96	8·15	1·18	3·65	—	3·16	99·99	3·62

*Torrensia* is named from the Torrens mine near Ville-Aure, where the mineral occurs with rhodonite and friedelite. It is compact, and light sepia to reddish-grey, becoming brown on exposure to the air ; the powder is pale greyish-rose, and is easily decomposed by acids. The mean (II) of two analyses gives the formula  $\text{MnSiO}_3, \text{MnCO}_3, \frac{1}{2}\text{H}_2\text{O}$ .

Homogeneous minerals containing both silicic and carbonic acids are of rare occurrence ; thaumasite and cancrinite are examples.

L. J. S.

**Deposition of Barium Sulphate as a Cementing Material of Sandstone.** By FRANK CLOWES (*Proc. Roy. Soc.*, 1899, **64**, 374—377).—Some years ago, a certain sandstone occurring near Nottingham was found to contain 33—50 per cent. of barium sulphate, which evidently served to cement the sand grains together. The existence of the barium sulphate has now been explained by the discovery that the water from an artesian boring in the district contains barium chloride (White, this vol., ii, 420). This fact, together with the proximity of calcium sulphate veins, accounts for the peculiarly local occurrence of the sandstone referred to. J. C. P.

**Quenstedtite from Iowa.** By OTTO KUNTZE (*Amer. Geologist*, 1899, **23**, 119—121).—In the dry season of the year, the sandstone



walls beneath the overhanging ledges on the banks of a small creek near Montpelier, Muscatine Co., are encrusted with a sulphur-yellow material 1—2 inches in thickness. It is readily soluble in cold water, and effloresces on long exposure to the air. Sp. gr. 2.212;  $H = 2\frac{1}{2}$ . The mean of two analyses is,

SO <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Insol. (SiO <sub>2</sub> ).	H <sub>2</sub> O.	Total.
39.01	0.27	26.86	1.79	32.32	100.25

This agrees approximately with the formula of quenstedtite, namely,  $Fe_2(SO_4)_3 + 10H_2O$ . At 105°, there is a loss of 21.04 per cent., gradually increasing to 29.94 per cent. at 140°. The substance has been derived by the oxidation of pyrites, numerous specks of which occur in the sandstone. Such substances are of comparatively rare occurrence, and are only formed under favourable conditions.

L. J. S.

**Formation of Minerals in Magmas.** By JÓZSEF MOROZEWICZ (*Tsch. Min. Mitth.*, 1898, 18, 1—90, 105—240).—The numerous experiments were made on large amounts (up to 1 cwt. or more) of material heated in fire-clay crucibles in a Siemens' furnace. After fusion of the material in the hottest part (1600°) of the furnace, the crucibles were moved to successively cooler places (down to 500°), allowing the magmas to cool and crystallise slowly for several weeks or months. The materials used were rocks, or mixtures of minerals or pure chemicals, of known composition. Numerous (54) analyses were made of the resulting rocks and crystallised minerals.

*Formation of Corundum, Spinel, Sillimanite and Cordierite in Silicate-magmas* (compare Abstr., 1895, ii, 275).—In attempts to produce certain types of volcanic rocks, some of the resulting crystalline masses were found to contain much corundum and spinel, and this led the author to determine the chemical conditions under which these minerals were formed. In these cases, the magmas were all rich in alumina, and in the crystalline products the corundum and spinel were set in a ground-mass, consisting of olivine, magnetite, nepheline, anorthite and glass, with sometimes melilite, augite, hypersthene and labradorite. The corundum crystals are tabular in habit and reach a diameter of 1.5 mm.; the various colours—blue, red, yellow—may be explained by the presence of oxides of iron. The material contains 99.5—99.8 per cent. of alumina; sp. gr. 4.03. The spinel octahedra are colourless, yellow, green, or black, depending on the amount of iron; in five analyses, the composition varies from  $13MgAl_2O_4 \cdot MgFe_2O_4$  to  $MgAl_2O_4 \cdot 4FeAl_2O_4$ , &c.

After isolating the corundum and spinel by means of hydrofluoric and sulphuric acids, analyses of the ground-mass showed that in all cases the ratio of  $Al : M (=K_2, Na_2, Ca)$  is unity; the excess of alumina over this amount in the original magma has separated as corundum, or as corundum and spinel when magnesia and iron oxides are also present. Magmas of the composition  $MO, Al_2O_3, 2SiO_2$  (anorthite) and  $MO, Al_2O_3, 6SiO_2$  (albite), are therefore capable of dissolving excess of alumina, which crystallises out on cooling in the form of corundum. An anorthite magma dissolves about 5 per cent. of alumina (in the form of bauxite), and a nepheline magma about

29·5 per cent., whilst in an orthoclase magma it is almost insoluble. Excess of silica and alumina in an albite magma crystallises out as sillimanite, in colourless prisms, and corundum. Corundum also crystallises from sodium aluminate containing an excess of alumina; hence the formation of corundum is not connected with the acidity or basicity of the magma. From an andesitic magma with  $\text{MO} : \text{MgO} : \text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 0·9 : 1·25 : 7$ , there was a separation of cordierite and spinel with labradorite, augite, magnetite and glass, and the product closely resembled the cordierite-vitrophyrte from South Africa described by Molengraaff.

The conditions for the separation of these minerals are summarised as follows: In supersaturated aluminosilicate magmas of the general composition  $\text{MO}, m\text{Al}_2\text{O}_3, n\text{SiO}_2$  ( $n = \text{or} > 2$ ), the whole of the excess of alumina ( $m - 1$ ) separates out: (a) as corundum if no magnesia or ferrous oxide is present, and if  $n < 6$ ; (b) as sillimanite, or sillimanite and corundum, if  $n > 6$ . When the magmas are rich in magnesia and ferrous oxide, the excess of alumina separates out: (c) as spinel, or spinel and corundum, if  $n < 6$ ; and (d) as cordierite, or cordierite and one or more of the other minerals, if  $n > 6$ .

Natural magmas containing an excess of alumina are of comparatively rare occurrence: descriptions and analyses are given of some rocks of this type occurring as veins in the granites, &c., of the Ilmen Mountains, Urals. *Kyschtymite* is the name given to a corundum-anorthite rock from the Kyschty district; it contains 50–60 per cent. of corundum and some spinel. Corundum-pegmatite and corundum-syenite from the same region consist respectively of corundum and orthoclase, and of corundum, orthoclase and biotite; in both cases, the orthoclase (microperthite) contains a considerable amount of soda. Such magmas containing an excess of alumina crystallising out as corundum are analogous to magmas containing an excess of silica, which crystallises out as quartz, and on this is based a classification of rocks. In other cases, where a separation of corundum, spinel, sillimanite and cordierite has taken place, there has been an absorption by the magmas of clay-slate at the contacts.

*Composition of Pyroxene from Silicate-fusions.*—Analysis I is of colourless crystals of enstatite, isolated from a magma having the composition of a basalt rich in magnesia. II (contains also a trace of  $\text{TiO}_2$ ) of augite crystals 1·5 mm. long, from a magma having the composition of a melilite-basalt. III (contains also  $\text{MnO}$ , 4·08 per cent.) of reddish-brown, prismatic crystals of augite from a fusion containing also huiyne, anorthite and magnetite; it contains, as shown by the analysis, 73 per cent. of Tschermak's hypothetical molecule,  $\text{MR}_2\text{SiO}_6$ , and it is more readily decomposed by hydrochloric acid than other pyroxenes. IV and V of alkali-augite, forming spherulites in quickly cooled basalt magmas.

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	Total.	Sp. gr.	Extinction on (010).
I.	53·07	4·12	6·08	0·94	2·85	33·75	—	—	100·81	3·087	0°
II.	46·93	6·76	10·82	0·70	20·00	12·70	trace	1·72	99·63	3·177	45
III.	30·87	13·82	25·35	1·12	22·17	1·54	0·43	1·51	100·89	> 3·18	8
IV.	53·72	7·87	7·19	5·17	8·70	5·73	1·10	10·03	99·51	2·886	18
V.	58·91	10·81	7·12	1·86	10·12	4·34	1·00	4·98	99·14	2·724	10

All these pyroxenes can be expressed as isomorphous mixtures of three silicates; the metasilicate  $M''SiO_3$ , Tschermak's hypothetical molecule  $M''R'''_2SiO_6$ , and the ægirite-jadeite molecule  $M''R'''_2Si_4O_{12}$ . The optical characters vary with the composition, the angle of extinction on  $b(010)$  decreasing with an increase in the amount of  $MR_2SiO_6$  and  $MR_2Si_4O_{12}$ ; the pure compound,  $MR_2SiO_6$ , would be expected to be orthorhombic.

In magmas rich in silica (>50 per cent.) and alkalis, the ægirite-jadeite molecule combines with the metasilicate, whilst in more basic magmas Tschermak's molecule takes its place. In magmas with about 50 per cent. of silica and poor in alkalis, orthorhombic pyroxenes separate when  $(MgO + FeO) : CaO$  equals or exceeds 3 : 1, whilst monoclinic pyroxene separates when this ratio is less than 3 : 1.

Wollastonite, in white, acicular crystals several cm. long, was found in the lower layers of ordinary glass, which had remained for a considerable length of time in contact with the hearth of the furnace, and were richer in lime than the upper layers. The crystals are elongated parallel to the axis of symmetry; analysis gave the formula  $CaSiO_3$ ; sp. gr. 2·8075.

*Synthesis of Nosean, Häüyne, Sodalite and Lagoriolite* (compare Abstr., 1893, ii, 19, 422).—Nosean, as white, grey, or blue isotropic dodecahedra and rounded grains, was formed when mixtures of kaolin and soda, or of kaolin, calcium carbonate and gypsum, were fused at a red heat ( $600^\circ$ ) for several days with excess of sodium sulphate. Five analyses of the material give the formula  $3(Na_2Al_2Si_2O_8) + Na_2SO_4$ , with, in some cases, a little sodium replaced by calcium; this formula also expresses the composition of natural nosean better than the usually accepted formulæ  $2(Na_2Al_2Si_2O_8) + Na_2SO_4$ , and  $3(Na_2Al_2Si_2O_8) + 2Na_2SO_4$ . The blue colour of the crystals is due to the presence of sulphides, probably iron sulphide.

Häüyne was not formed by fusing mixtures of the composition of häüyne with sodium sulphate. It was produced together with augite (anal. III. above) in a magma having the composition of häüyne-basalt.

Sodalite in white dodecahedra or grains was formed when kaolin or nepheline was fused with soda and excess of sodium chloride. Analyses give the formulæ  $2(Na_2Al_2Si_2O_8) + NaCl$  and  $3(Na_2Al_2Si_2O_8) + 2NaCl$ , both of which agree with natural sodalites.

*Lagoriolite* (soda-garnet) is the name given to a new product obtained by fusing at a dark red-heat mixtures of silicic acid and hydrargillite,  $Al(OH)_3$ , with sodium and calcium sulphates and carbonates. The square plates are flattened cubes which are either isotropic or birefringent with twin lamellæ. Analyses give the formula  $3(Na_2Ca)O, Al_2O_3, 3SiO_2$  with  $Na_2O : CaO = 3 : 2$ ; in one analysis, there is only a trace of calcium, and in all there are small quantities of sulphuric anhydride. This is the garnet formula, and the substance forms a connecting link between the garnet and the nosean groups. The largest amount of alkali yet found in natural garnet is 4·22 per cent. in melanite from the phonolite of Oberschaffhausen.

*Liparite magmas*.—Acid magmas do not readily crystallise, and as a rule they solidify to a glass. When, however, the experimental

magmas have crystallised, the excess of silica has separated as tridymite, or in a prismatic modification the characters of which are as yet unknown. A liparite magma, fused with 1 per cent. of tungstic acid, gave crystals of quartz, biotite and sanidine proving that the essential constituents of granite can be formed by dry fusion.

A list of minerals which have been formed artificially by the author includes all the important rock-forming minerals except hornblende, and the crystallised fusions represent almost all the known types of aluminosilicate rocks. The structure of these artificial rocks depends on the chemical composition of the magma and on the rate of cooling. The order in which the various minerals separate from the magmas is discussed; it does not depend, as has been stated, on the fusibility or basicity of the minerals, but on their solubility and the relative amounts in which they are present in the solution. Several cases are noticed in which there has been a differentiation in the artificial magmas, as shown by a separation into layers of different chemical composition and specific gravity.

Incidentally, the following analyses are given of material used in the experiments: A, (by F. Dutkowski), of kaolin from Schneeberg; B. nepheline, from Låven, Norway.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> . Fe <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
A.	45.75	40.17	0.20	—	—	13.98	100.10
B.	44.51	33.38 —	0.45	5.50	15.69	1.37	100.90.

L. J. S.

**Asbestos.** By PAUL KERSTING (*Chem. Centr.*, 1898, ii, 125; from *Chem. Ind.*, 21, 171—174).—The best commercial asbestos is from North Italy; Canadian and South African are now coming into use. Analyses I and II are of Canadian [chrysotile], and III of blue South African [crocidolite]. For I and II, the formula is given as  $\text{MgSiO}_3, \text{Mg}_2\text{SiO}_4 + 2\text{H}_2\text{O}$ , and for III,  $(\text{Mg}, \text{Fe})\text{SiO}_3 + \text{H}_2\text{O}$ . When treated with hydrochloric acid, there is dissolved 41.24 per cent. of I, 37.48 of II, and 12.62 of III. The South African is softer and finer than the Canadian, but it is less refractory and falls to pieces when ignited.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	H <sub>2</sub> O.	Total.
I.	39.04	trace	0.25	2.10	0.51	42.57	0.09	0.22	—	0.10	15.20	100.08
II.	41.56	3.42	0.41	6.67	0.83	33.38	0.11	0.30	—	0.08	13.15	99.91
III.	43.61	0.21	16.57	12.15	0.89	7.02	3.06	2.14	0.06	0.06	14.30	100.07

L. J. S.

**Thalite and Bowlingite from Lake Superior.** By NEWTON H. WINCHELL (*Amer. Geologist*, 1899, 23, 41—44).—Thalite was described in 1852 as occurring in cavities in trap at several places on the north shore of Lake Superior. It is soft with a soapy feel, and is dirty white or grey; it is easily gelatinised by hydrochloric acid. Sp. gr. 2.20. Thin sections show a confused vermicular aggregate, sometimes with bands formed of minute transverse fibres; the fibres show a

positive bisectrix parallel to their length with a small axial angle. Analysis by L. B. Pease gave,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
42.38	7.37	2.65	23.29	5.52	0.19	0.36	18.18	99.94

At 100°, there is a loss of 10.38 per cent.

Pseudomorphs after olivine occurring in the same rocks are supposed to be bowlingite; the optical characters of this are described.

L. J. S.

**Thalénite, a new Mineral.** By CARL BENEDICKS (*Geol. För. Förh.*, 1898, 20, 308—312; and *Bull. Geol. Inst. Univ. Upsala*, 1899, 4 (1898), 1—15).—The new mineral occurs, massive and in crystals, with fluocerite, gadolinite and allanite in quartz at Österby in Dalecarlia, Sweden. It is flesh-red and translucent, with a greasy lustre. Fracture uneven to splintery; brittle; no cleavage;  $H = 6\frac{1}{2}$ . Approximate measurements of the dull, monoclinic crystals gave [ $a:b:c = 1.154:1:0.602$ ;  $\beta = 80\frac{1}{2}^\circ$ ]. Optically negative, axial plane  $\perp b(010)$ ,  $\beta_{\chi a}$  nearly  $\perp a(100)$ ,  $2V = 67^\circ 35'$ ,  $\alpha = 1.7312$ ,  $\beta = 1.7375$ ,  $\gamma = 1.7436$  (Na). The material is easily decomposed, with separation of gelatinous silica, by dilute hydrochloric acid. The mean of five partial analyses made on fresh, transparent material of sp. gr. 4.227 is given under I; formula,  $H_2O, 2Y_2O_3, 4SiO_2$ . The molecular weight of the yttrium earths is 245.3; the absorption spectrum of the nitrates shows the presence of erbium, holmium and didymium. The gas liberated when the mineral is heated or treated with acids was examined spectroscopically and found to contain nitrogen and helium.

	SiO <sub>2</sub> .	Y <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	BeO.	CaO.	MgO.	Na <sub>2</sub> O.	SnO.	H <sub>2</sub> O.	CO <sub>2</sub> .	Gas.	Total.
I.	29.88	63.35	0.30	0.45		0.49	0.21	0.26	0.23	2.08	1.04	1.40	99.69
II.	27.69	58.58	1.51	0.35		2.19	0.40	1.07	0.22	2.70	3.32	2.50	100.53
III.	30.89	63.91	0.25?	—		0.37	0.10	0.36	0.19?	1.54	Nil	1.96	99.57

Analysis II is of weathered thalénite; this is lighter in colour and softer; sp. gr. 3.945. Some organic matter is present, and to this the colour of the mineral is probably due.

Minerals allied to thalénite are yttrialite, rowlandite, and kainosite. There are also analogies in the chemical formulæ and crystal angles of thalénite and laumontite.

In an appendix to the second paper, new material is described. This is yellow in colour. It is more transparent, has a stronger lustre and weaker birefringence;  $\mu = 1.713$ , sp. gr. 4.11—4.16; fracture conchoidal. Analysis III shows it to be a purer form of thalénite. The molecular weight of the yttrium earths is 246.2.

L. J. S.

[Analyses of Felspars.] By FRANZ LOEWINSON-LESSING (*Jahrb. f. Min.*, 1899, ii, Ref. 232—238; from *Travaux Soc. des Nat. St. Pétersbourg*, 1898, 26, livr. 5, 404 + xl. pp. (Russ.) + 7 pp. Résumé (French).—The following analyses of felspars are given in a petrographical paper dealing generally with a chemical classification of rocks, and on

the eruptive rocks of a portion of the Central Caucasus: numerous analyses of rocks are also given.

I, partly pelitised felspar from porphyritoid; II, albite from an adinole; III, pelitised felspar; IV, felspar in porphyrite from the Basboika River, Urals; V—VII, pelitised felspar; VIII, felspar in gabbro from Höllmühle, near Penig; IX, in gabbro-diorite from Kühler Grund, near Eberstadt; X, in gabbro from Thalhörn, Vosges; XI, orthoclase from Baveno granite:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Loss on ignition.	Total.
I.	50·09	29·64	—	—	14·09	1·11	—	—	5·43	100·36
II.	64·18	21·37	—	—	—	—	—	11·30	0·45	97·30
III.	52·00	22·95	0·21	0·47	18·50	0·44	0·42	2·40	3·24	100·63
IV.	50·86	24·71	0·95	1·56	9·20	0·48	2·80	4·12	5·41	100·09
V.	45·11	28·58	1·28	—	18·24	1·27	0·30	2·52	2·97	100·27
VI.	48·15	32·38	—	—	16·09	0·47	0·38	2·13	1·18	100·78
VII.	59·60	23·66	—	—	4·57	—	6·21	3·72	1·80	99·56
VIII.	50·52	31·37	—	—	13·25	—	—	4·13	0·55	99·82
IX.	53·78	31·19	—	—	8·02	0·37	0·84	5·00	0·88	100·08
X.	53·22	29·85	—	—	4·53	1·30	3·33	4·70	2·96	98·89
XI.	67·66	18·73	—	—	—	—	8·43	3·75	0·67	99·24

In several so-called "kaolinised" plagioclases, it is shown that the alteration product is not kaolin, but a mixture of various hydrated silicates of aluminium and magnesium, zeolites, &c.; for this mode of alteration of felspar the term pelitisation is proposed. L. J. S.

**Constitution of Tourmaline.** By FRANK W. CLARKE (*Amer. J. Sci.*, 1899, [iv], 8, 111—121).—The author argues in favour of the formula of tourmaline,  $2[\text{Al}(\text{SiO}_4)_3\text{R}''_2(\text{Al}\cdot\text{BO}_2)]:\text{Al}(\text{BO}_3)\text{R}'_2$ , proposed by him (*Abstr.*, 1897, ii, 52), as opposed to the formula recently given by Penfield and Foote, namely,  $(\text{H}, \text{R}', \&c.)_9\text{Al}_3(\text{B}\cdot\text{OH})_2\text{Si}_4\text{O}_{19}$  (this vol., ii, 304). Reducing both formulæ to the ultimate acids, they become respectively  $\text{H}_{20}\text{B}_3\text{Si}_6\text{O}_{31}$  and  $\text{H}_{30}\text{B}_3\text{Si}_6\text{O}_{31\frac{1}{2}}$ . The small difference between these formulæ hardly amounts to more than the uncertainties of the analyses. Clarke's formula expresses the relation between the micas and tourmaline, and it is shown to agree closely with several of Riggs' analyses. Analyses from which Penfield and Foote's formula may be deduced may also be made to agree with Clarke's formula by assuming the presence of the basic divalent group  $\text{Al}\cdot\text{OH}$  or  $\text{AlF}$ , and by replacing some Ca by NaH; and the few analyses in which boric acid is low may be explained by partial replacement of  $\text{Al}\cdot\text{BO}_2$  by  $\text{Al}\cdot\text{OH}$  and  $\text{AlF}$ . [Clarke's acid,  $\text{H}_{20}\text{B}_3\text{Si}_6\text{O}_{31}$ , is identical with that recently deduced by Rheineck (this vol., ii, 601).]

L. J. S.

**Composition of Moldavite.** By CONRAD H. VON JOHN (*Verh. k.k. geol. Reichs.*, 1899, 179—182. Compare *Abstr.*, 1896, ii, 434).—F. E. Suess (*Verh. k.k. geol. Reichs.*, 1898, 387; *Anzeiger Akad. Wiss. Wien*, 1898, No. XXIV.) has recently given reasons, mainly based on the peculiar surface markings, for considering moldavites to be of cosmic origin, and he concludes that they represent a hitherto unrecognised type of aerolites. The following analyses are given of the material examined by Suess: I, moldavite from Budweis in Bohemia; II and III, from Trebitsch in Moravia.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total
I.	82·68	9·56	—	1·13	0·18	2·06	1·52	2·28	0·63	—	100·04
II.	78·61	12·01	0·16	3·09	0·11	1·62	1·39	3·06	0·44	—	100·49
III.	77·96	12·20	0·14	3·36	0·10	1·94	1·48	2·70	0·61	—	100·49
IV.	52·32	0·30	—	1·20	1·02	17·52	3·60	22·84	0·24	0·80	99·84

Analysis IV is of material from Netin, Moravia, which was considered by Suess to be an artificial glass since it differed from true moldavite in colour and the characteristic surface markings; the analysis also shows it to be quite distinct. Nine earlier analyses of moldavite are quoted, and there is seen to be very little variation in composition.

L. J. S.

**Riebeckite and Ægirine in Granite from Turcoaia, Roumania.** By L. MRAZEC (*Bull. Soc. Sci. Bucarest*, 1899, 8, 106—111).—A grey, medium-grained granite extensively quarried at Mt. Jacob Deal, near Turcoaia, in the district of Dobrogea [Dobrudscha], contains magnetite, allanite?, zircon, ægirine, riebeckite, albite, anorthoclase, orthoclase, quartz, hematite, limonite, epidote and chlorite. The riebeckite occurs as black prisms sometimes 2 cm. long; it is strongly pleochroic, and the angle of optical extinction on (010) is 5°. Chlorite and limonite are formed by its alteration. Analysis of impure material gave,

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
[45·69]	7·01	14·33	17·62	3·24	4·28	1·77	4·62	0·99	0·45	100·00

L. J. S.

**Alteration Products of Magnesia-mica; Variation of the Optical Characters with the Composition.** By EBERHARD ZSCHIMMER (*Jahrb. f. Min.*, 1899, ii, Ref. 210—214; from *Inaug.-Diss. Jena*, 1898).—The following analyses are given of lepidomelane, in various stages of alteration, from the granite of the Schneidemüllerskopf, near Ilmenau, in Thuringia; optical determinations are also given. The fresh mica has the composition of lepidomelane, and all the altered forms can be expressed as mixtures of Tschermak's two molecules, H<sub>2</sub>K(Al,Fe)<sub>3</sub>Si<sub>3</sub>O<sub>12</sub> and Mg<sub>6</sub>Si<sub>3</sub>O<sub>12</sub>.

SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	FeO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Total	Sp. gr.
32·75	1·85	14·79	23·53	10·25	3·09	5·35	4·30	—	3·79	99·70	3·09
35·38	0·81	15·63	16·27	12·30	1·59	8·06	5·34	0·22	5·38	100·98	3·00
35·69	0·14	17·85	18·62	11·83	2·22	4·64	3·27	0·39	5·82	100·47	2·94
33·93	1·23	16·02	17·75	13·53	1·85	3·63	3·29	—	7·80	99·08	2·85
35·88	1·25	18·88	14·97	13·66	1·34	3·69	2·25	—	7·73	99·65	2·82
36·87	1·61	21·21	11·97	12·34	1·78	3·63	2·36	—	7·64	99·41	2·78

With progressive alteration (or "bleaching") there is a separation of iron as ferric oxide, and a replacement of potash by water; at the same time, the specific gravity, pleochroism, and indices of refraction decrease, whilst the optic axial angle increases.

A connection is traced between the optic axial angle of various micas and the chemical composition. The position of the optic axial plane in the two classes of micas does not depend on the chemical composition, but is possibly connected with a kind of dimorphism.

L. J. S.

**Sandstone from Augusta Co., Virginia.** By W. W. MILLER, jun. (*Amer. Chem. J.*, 1899, 22, 216—217).—The sandstone, which consists of angular fragments interspersed with small seams of clay, possesses the peculiar property of becoming firm and compact when it is laid and beaten down for a pathway and left undisturbed. Analysis gave

	SiO <sub>2</sub> (amor- phous, free.)	SiO <sub>2</sub> (com- bined.)	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O at 100°.	H <sub>2</sub> O by ig- nition.	Total.
Clay...	0.53	63.68	24.23	0.94	3.57	1.25	4.04	0.77	0.49	4.83	99.29
Rock..	0.00	96.72	2.37	0.00	0.46	0.00	0.00	0.19	0.00	0.26	100.00

These results do not explain the peculiar packing power of the material, which must, therefore, be attributed to physical causes. W. A. D.

**The Parent-rock of the Diamond in South Africa.** By THOMAS GEORGE BONNEY (*Proc. Roy. Soc.*, 1899, 65, 223—236).—In the “blue ground” of the Newlands mines, West Griqualand, about 40 miles N.W. of Kimberley, are rounded boulders of eclogite (a holocrystalline, igneous rock composed of garnet and diopside), which occasionally contains colourless octahedra of diamond apparently as an original constituent. It has long been recognised that the diamonds have not been formed *in situ* in the “blue ground,” but until now the only mineral found intimately associated with them is garnet. The water-worn character of the eclogite boulders proves that the “blue ground” is not of igneous origin, but a true breccia produced by the destruction of various rocks, including the eclogite which has contributed the diamonds to the mixture. L. J. S.

**Rhyolites of the Hauraki Goldfields, New Zealand.** By JAMES PARK and FRANK RUTLEY, with Analyses by PHILIP HOLLAND (*Quart. Journ. Geol. Soc.*, 1899, 55, 449—469).—A geological and petrographical description is given of the Pliocene rhyolites of the Hauraki goldfields. The gold-bearing rocks are andesites. Analysis I is of a pale lithoidal rock from Omahu, consisting almost exclusively of small spherulites with some quartz, sanidine and oligoclase. II is of a pale greyish-white or yellowish rhyolite from Waihi, with numerous minute crystals of oligoclase and andesine, with some sanidine and labradorite:

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	BaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	SO <sub>3</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
I.	77.59	0.63	12.75	0.67	Nil	0.04	0.10	0.16	3.99	2.56	0.07	1.54	100.10	2.511
II.	73.08	0.62	13.50	2.60	0.13	1.07	0.06	0.15	3.19	3.95	0.12	1.33	99.80	2.514

Also traces of MnO and P<sub>2</sub>O<sub>5</sub>.

L. J. S.

**Clay from Russia.** By R. THAL (*Jahrb. f. Min.*, 1899, ii, Ref., 210; from *Chem. Zeit.*, 1898, 690).—Thirteen analyses are given of clay from the Gov. Novgorod. L. J. S.

**Origin of the Gases Evolved on Heating Mineral Substances, Meteorites, &c.** By MORRIS W. TRAVERS (*Proc. Roy. Soc.*, 1898, 64, 130—142).—Some minerals containing water, carbonic anhydride, and ferrous oxide give off hydrogen and carbonic oxide when heated, but not when decomposed with dilute sulphuric acid, indicating that the gases are not present in the mineral in the free



state. The amount of hydrogen and carbonic oxide liberated on heating is proportional to the quantity of water, carbonic anhydride, and ferrous oxide in the mineral; hence it is probable that these substances interact according to the equations  $2\text{FeO} + \text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + \text{H}_2$  and  $2\text{FeO} + \text{CO}_2 = \text{Fe}_2\text{O}_3 + \text{CO}$ .

A specimen of Peterhead granite when heated gave off carbonic anhydride, carbonic oxide, and hydrogen, and further investigation showed that the greater part of the carbonic anhydride is derived from the quartz, whilst the hydrogen comes chiefly from the mica and feldspar. The carbonic anhydride is probably contained in cavities in the quartz, and the absence of hydrogen in the quartz is against the view that it also is contained in cavities. Analysis showed that the feldspar contained both free iron and ferrous oxide.

When heated in a sealed tube with copper sulphate and water, meteoric iron gave only traces of hydrogen and carbonic oxide, whilst a considerable quantity of these gases was evolved when the iron was heated in a vacuum. It thus appears that the gases obtained by heating meteorites are not present as such, but are produced by the interaction of their non-gaseous constituents.

Microscopic examination of minerals which yield helium fails to reveal the presence of cavities, and on certain grounds it is probable that the helium is combined with some constituent of the mineral. The gas is associated with particular minerals, and in some cases the liberation of helium is accompanied by a considerable development of heat. The quantity of helium obtained from cleveite by treatment in an exhausted tube with 30 per cent. sulphuric acid is about double that obtained by merely heating the mineral, and this suggests the possibility of helium being in a state of binary combination, and being evolved according to the equation  $\text{XHe}_2 = \text{XHe} + \text{He}$ . If the helium were combined with a metal, treatment of the mineral with sulphuric acid would liberate it as a hydride, which would probably be an unstable compound; this may account for the fact that both cleveite and fergusonite yield hydrogen when decomposed with sulphuric acid.

J. C. P.

**Meteorite from Mighei, Russia.** By PETR G. MELIKOFF and W. KRSCHISCHANOWSKY (*Jahrb. f. Min.*, 1899, ii, Ref. 30—31; from *J. Russ. Chem. Soc.*, 1896, 28, 429, 651—657. Compare Abstr., 1890, 346).—Analyses of this stone, which fell at Mighei, Kherson, in South Russia, on June 18th, 1889, gave I for the portion soluble in water, II for the portion soluble in hydrochloric acid, and III for the insoluble portion.

	$\text{SiO}_2$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{Al}_2\text{O}_3$ .
I.	0·03	0·17	0·25	—	—	0·68	0·08	—
II.	24·29	1·85	18·10	22·63	0·55	1·25	0·13	1·38
III.	54·27	4·35	29·68	3·42	1·73	2·02	0·62	4·08
	S.	$\text{SO}_3$ .	$\text{S}_2\text{O}_3$ .	$\text{FeS}$ .	Fe.	Ni, Co.	Cl. org. matter.	
I.	—	0·85	0·12	—	—	—	0·04	0·53
II.	3·52			0·46	2·94	1·01	—	—

There is also 1·62 per cent. of chromite, and some amorphous carbon and organic matter. L. J. S.

**Meteorite from Zmjenj, Russia.** By PETR G. MELIKOFF (*Jahrb. f. Min.*, 1899, ii, Ref., 31—33; *J. Russ. Chem. Soc.*, 1896, 28, 114, 299—307).—Analysis of the stone which fell at Zmjenj, Minsk, in West Russia, in August, 1858, gave I for the portion soluble in hydrochloric acid and II for the insoluble portion; in I also FeS, 1·32; Fe<sub>2</sub>Ni, 0·32; P<sub>2</sub>O<sub>5</sub>, 0·08.

	SiO <sub>2</sub> .	MgO.	CaO.	FeO.	MnO.	Al <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	FeCr <sub>2</sub> O <sub>4</sub> .	Total.
I.	9·72	1·20	3·98	1·03	0·41	6·27	0·13	0·56	—	25·02
II.	38·46	15·61	1·86	13·45	1·76	1·79	0·25	1·19	0·56	74·93

The mineralogical composition is: Anorthite, 23·3; bronzite, 74·36; troilite, 1·32; chromite, 0·56; nickel-iron, 0·32 per cent. In the ground-mass of anorthite and bronzite are porphyritic crystals of yellow bronzite with the composition 2MgSiO<sub>3</sub>.FeSiO<sub>3</sub>. The crust of the meteorite contains magnetite which has originated by the fusion of the bronzite. L. J. S.

**Meteoric Iron from Tombigbee River, Alabama, U.S.A.** By WARREN M. FOOTE (*Amer. J. Sci.*, 1899, [iv], 8, 153—156).—Six masses, weighing in the aggregate 43795 grams, were found between (about) 1859 and 1886 in a north and south line, nine miles in length, near the Tombigbee River in Choctaw and Sumter Counties, Alabama. One of the masses shows minute Widmanstätten figures on the etched surface; another shows schreibersite in large, graphic characters, and the plessite in places presents a glistening, frosted effect. Analysis by J. E. Whitfield of the mass showing the Widmanstätten figures gave

Fe.	Ni.	Co.	P.	C.	S.	Total.
95·02	4·11	0·40	0·324	0·161	trace	100·015.

L. J. S.

**Mineral Water from Árva-Polhora, Hungary.** By WILHELM KALMANN and MORIZ GLÄSER (*Tsch. Min. Mitth.*, 1899, 18, 443—446).—Water for the baths at Árva-Polhora, Hungary, is clear and faint yellow; it turns litmus paper violet, and has a faint odour resembling that of iodiform; on long standing in the air, a flocculent, rusty-coloured precipitate is produced. Sp. gr. at 15° = 1·02178. A litre of the water (at 15°) contains the following constituents (in grams): K<sub>2</sub>O, 0·15084; Na<sub>2</sub>O, 14·74420; Li<sub>2</sub>O, 0·14451; CaO, 0·46307; BaO, 0·02746; SrO, 0·12332; MgO, 0·14812; FeO, 0·05603; Cl, 17·66109; Br, 0·11333; I, 0·04109; SO<sub>3</sub>, 0·03071; CO<sub>2</sub>, 0·23650; P<sub>2</sub>O<sub>5</sub>, 0·00378; B<sub>2</sub>O<sub>3</sub>, 0·19382; SiO<sub>2</sub>, 0·00865; organic matter, 0·04781; fixed solids, 30·14185. The amounts of some of these constituents differ considerably from those shown in the earlier analysis of this water by C. von Than. L. J. S.

**Water of Bagnoli, Tuscany.** By RAFFAELE NASINI and ROBERTO SALVADORI (*Gazzetta*, 1899, 29, ii, 161—180).—This water, which issues at a constant temperature of 21°, is very clear, has a pleasing taste, and is faintly acid to litmus paper. It has a sp. gr. 1·00014

at  $12^{\circ}/4^{\circ}$ , its freezing point is  $-0.007^{\circ}$ , and its electrical conductivity 0.1243 at  $25^{\circ}$ . When allowed to stand in an open vessel for a long time, a yellowish-white, flocky deposit is obtained, and, on prolonged boiling, beautiful laminae of gelatinous silica are formed. The water is bacteriologically pure. On analysis, the following results were obtained (grams per litre): Li, 0.000005; K, 0.00382; Na, 0.00935; Mg, 0.004175; Ca, 0.00867; Al, 0.00064; Fe, 0.00041;  $\text{SO}_4$ , 0.02952;  $\text{HCO}_3$ , 0.03298; Cl, 0.00776;  $\text{SiO}_2$ , 0.07336; and  $\text{TiO}_2$ , 0.000025; total, 0.170745. There are present also traces of rubidium, manganese, strontium, iodine, phosphoric and boric acids, and organic matter. The dissolved gases are 4.10 c.c. of oxygen and 13.16 c.c. of nitrogen per litre; the water has a permanent hardness 5.00, and a temporary hardness 0.33, expressed in French degrees. Its therapeutic and antiseptic properties are probably due to the relatively large amount of silica.

T. H. P.

**Deposition of Sulphur and Pyrites from Carlsbad Thermal-water.** By JOSEF KNETT (*Jahrb. f. Min.*, 1899, ii, 81—84).—The small quantities of sulphur and pyrites deposited from Carlsbad thermal-water have probably originated in the reduction of sulphates by wood.

L. J. S.

**Mineral Water from the Stanislawia Spring, Galicia.** By VON DUNIN-WASOWICZ and J. HOROWITZ (*Chem. Centr.*, 1899, ii, 491; from *Pharm. Post.*, 32, 295—297, 307—309, 319—320).—The Stanislawia spring is in the Matkow forest, near Karlsdorf. One kilo. of the water contains, in grams:  $\text{NaHCO}_3$ , 2.589612;  $\text{FeH}_2(\text{CO}_3)_2$ , 0.024325;  $\text{MnH}_2(\text{CO}_3)_2$ , 0.001471;  $\text{CaH}_2(\text{CO}_3)_2$ , 0.918375;  $\text{BaH}_2(\text{CO}_3)_2$ , 0.097319;  $\text{SrH}_2(\text{CO}_3)_2$ , 0.215678;  $\text{NaCl}$ , 3.497792;  $\text{KCl}$ , 0.063051;  $\text{LiCl}$ , 0.004916;  $\text{NaI}$ , 0.000379;  $\text{NaBr}$ , 0.000603;  $\text{NaNO}_3$ , 0.000020;  $\text{Na}_2\text{SO}_4$ , 0.075956;  $\text{SiO}_2$ , 0.043350;  $\text{CO}_2$  (free), 2.157232; organic matter, 0.106650. Also traces of copper oxide, nickel oxide, cobalt hydroxide, rubidium chloride, caesium chloride, ammonium chloride, sodium arsenite, sodium borate, calcium phosphate, and calcium sulphide.

L. J. S.

**Periodic Analyses of the Rivers of the West Riding of Yorkshire.** By EDWARD HALLIWELL (*J. Soc. Chem. Ind.*, 1899, 18, 348—355).—This is a paper of great local interest, showing the variation in composition and pollution of several streams in Yorkshire. Complete tables are given.

L. DE K.

### Physiological Chemistry.

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**Taste in Relation to Chemical Composition.** By WILHELM STERNBERG (*Chem. Centr.*, 1899, i, 1216; from *Zeit. Verein. Rübenzuck.-Ind.*, 1899, 376—388).—Whilst the hydrocarbons themselves are colourless and tasteless, derivatives containing oxygen or nitrogen in certain groupings, for instance, as OH- or  $\text{NH}_2$ -groups, possess both colour, odour, and taste, the last only, however, when these groups are

combined with a positive alkyl or a negative carboxyl group respectively. The  $\text{NO}_2$ -group also confers the property of taste on compounds, and such groups are named "sapiophore." For a compound to have a sweet taste, it must contain at least two oxygen atoms, and every positive group must be united to a negative group, every alkyl group being combined with a hydroxyl group. Thus all polyatomic alcohols taste sweet. The introduction of positive groups, however, changes the sweet to a bitter taste (acetyl compounds of glucose). Aromatic sugars, such as phenyltriose, have a bitter taste. A certain regularity and symmetry of the arrangement of the groups is also a condition of sweetness. In the case of inorganic compounds, the property of a sweet or bitter taste is dependent on certain elements, and these elements the author arranges in a system. E. W. W.

**Physiology of Pregnancy.** By ALBERT CHARRIN and GUILLEMONAT (*Compt. rend.*, 1899, 128, 1180—1182).—Inanition in pregnant guinea pigs was compared with that in normal animals. In all cases, a few c.c. of a saline solution were injected daily under the skin. The pregnant animals waste more rapidly, excrete less urine and less urea, develop less heat, are poorer in iron, and offer more marked alterations of structure than the others. W. D. H.

**Iron in the Spleen during Pregnancy.** By ALBERT CHARRIN (*Compt. rend.*, 1899, 128, 1614—1615).—The determinations of iron in the spleen confirm the fact, previously recorded by others, that during pregnancy the iron diminishes in that organ, and passes to the fetus. Microchemical examination confirms this result. W. D. H.

**Influence of the Grape Cure on Human Metabolism.** By B. LAQUER (*Chem. Centr.*, 1899, i, 893; from *Centr. inn. Med.*, 20, 193—203).—During the grape cure, there is proteid-sparing, and in consequence, a putting on of proteid. The aromatic substances contained in grapes which are not too sour produce a lessening of uric acid, and cause it to be separated in a relatively soluble form; this depends on the relationship between the mono- and di-sodium phosphates. Hippuric acid is not markedly influenced. Large quantities (4—5 pounds) of grape juice increase proteid putrefaction, and cause a rise in the ethereal hydrogen sulphates of the urine. W. D. H.

**Metabolism in Inanition.** By FRIEDRICH N. SCHULZ (*Pflüger's Archiv*, 1899, 76, 379—410).—During inanition, or when the nutrient given is insufficient, as when carbohydrate alone is given, there is, on the day or two preceding death, an increase in the nitrogen excreted in the urine. This rise, which has been noted by previous observers, is usually accompanied with albuminuria; the nitrogen of the albumin is not, however, sufficient to account for the total increase of nitrogen, but it probably is an indication of the breakdown of the kidney cells. The experiments recorded on rabbits and dogs show that this ante-mortem rise of nitrogen is not a criterion that the animal has reached an absolute minimum of fat, although probably the fat which is left is, in the condition of the animal, not capable of proper utilisation. W. D. H.

**Metabolic Experiments with Proteids containing, or not containing, Phosphorus.** By H. ZADIK (*Pflüger's Archiv*, 1899, 77, 1—21).—Experiments were carried out on dogs, and the course of their metabolism followed when a proteid containing phosphorus (casein) was given; this was compared with what occurs when a phosphorus-free proteid (edestin) was administered. The animals receiving casein showed that they are able to absorb and assimilate the organic phosphorus, but that the living cells are not able to manufacture phosphorus-holding materials from inorganic phosphates and proteids which are free from phosphorus.

In a further comparison of the two phosphorus-holding proteids, vitellin and casein, it was found that the nitrogenous balance during the administration of the former is the more favourable. W. D. H.

**The Course of Peptic Proteolysis Examined Quantitatively.** By E. ZUNZ (*Zeit. physiol. Chem.*, 1899, 28, 132—173. Compare this vol., ii, 504).—Artificial gastric digestion experiments were carried out with purified proteids such as crystallised egg-albumin and serum-albumin. The digestion was stopped at varying intervals, and the products separated by fractional precipitation with zinc sulphate. The results represented in curves show much the same course in all cases; as the primary products disappear, the secondary products increase. The primary products are acid-albumin, proto- and hetero-proteose, and deuto-proteose *B*. The secondary products are the remaining deuto-proteoses, peptone, and a number of unknown substances which do not give the biuret reaction, as well as ammonia and amido-substances. A portion of these unknown substances must be regarded as primary products. W. D. H.

**Metabolism in the Submaxillary Gland.** By YANDELL HENDERSON (*Amer. J. Physiol.*, 1899, 3, 19—25).—In the submaxillary gland, proteid metabolism is more or less distinct from the processes of combustion and liberation of energy; this accords with Heidenbain's hypothesis that the elimination of water and salts, and that of the organic constituents of saliva, are controlled by different mechanisms. On the one hand, in proteid metabolism controlled by *trophic* nerve-fibres, anabolism occurs coincidentally with katabolism, for the nitrogen in the saliva is greater than that lost by the active gland; the gland tends to remain in nitrogenous equilibrium. On the other hand, the processes controlled by the *secretory* nerve-fibres are apparently performed at the expense of a combustion of carbonaceous material stored within the cells during rest, to become the source of heat and secretory work. W. D. H.

**Influence of the Removal of the Large Intestine on Metabolism in Dogs.** By VAUGHAN HARLEY (*Proc. Roy. Soc.*, 1898—1899, 64, 77—88; 255—307).—In normal dogs, an increase of fat in the food leads to a decrease of urine and urinary nitrogen. After partial removal of the large intestine, the results are similar, except that the fæces are not so greatly increased. Total removal of the large intestine leads to the same effect on the urine, but the nitrogen and fat in the fæces are not influenced; the water in the fæces rises.

Removal of the large intestine does not affect the absorption of carbohydrates, or the breaking up and absorption of fat; but the absorption of proteids is lessened by about 10 per cent. In these animals, large quantities of bile pigment with little or no urobilin are found in the faeces. The alkaline sulphates of the urine are diminished by an increase of fat in the food, but the ethereal hydrogen sulphates are not affected; the same is true for normal dogs. The secretion of the large intestine contains proteids, fats, and salts, but no pigment; the small intestine secretes pigment. W. D. H.

**Intestinal Absorption.** By E. WAYMOUTH REID (*Proc. Roy. Soc.*, 1899, 65, 94—95).—The physiological activity of the intestinal epithelium in absorption is demonstrated by the absorption by an animal of its own serum or plasma under conditions in which filtration, osmosis, and adsorption are excluded; and by the cessation or lessening of the absorption when the epithelium is removed or injured, in spite of the fact that facilities for osmosis and filtration are thereby increased. The chief factor in the absorption of peptone is assimilation (or adsorption) by the cells, whereas in the absorption of sugar, diffusion, variable by the permeability of the cells (and so probably related to their physiological condition), is the main factor. Alcohol stimulates the cells, bile does not. Details are added which show differences in different parts of the intestinal canal. The cells take up organic solids most slowly, then water, then inorganic salts. W. D. H.

**Absorption of Iodine Oils.** By ROBERT RÖSEL (*Pflüger's Archiv*, 1899, 77, 22—25).—Experiments on human beings show that the iodine of iodised fats is more quickly absorbed than is the iodine from inorganic compounds. In 51—58 hours, from 43 to 79 per cent. of the iodine was recovered in the urine. W. D. H.

**Artificial Nutrition of a Normal and of an Atrophic Infant.** By MAX RUBNER and OTTO HEUBNER (*Zeit. Biol.*, 1899, 38, 315—398).—A lengthy and detailed account of the metabolism and heat formation in two infants brought up by hand; one child was healthy, the other atrophic and feeble. The points of difference are numerous, as would be expected. W. D. H.

**Formation of Fat from Proteid in the Cat.** By MAX CREMER (*Zeit. Biol.*, 1899, 38, 309—314).—By feeding cats on flesh free from fat and glycogen, carbon is put on in too large a quantity to be accounted for as glycogen. The opinion that it is present as fat is defended in view of Pflüger's criticisms on this point. W. D. H.

**The Source of Fœtal Fat. I.** By MARTIN THIEMICH (*Chem. Centr.*, 1899, 939; from *Centr. Physiol.*, 12, 850—852).—The fat of new born children differs considerably in composition. In order to see whether this is due to the mother's diet, one dog during the pregnant period was given a cocoa fat with low iodine number (8), and another linseed oil (iodine number, 120). There was, however, no difference in the composition of the fat of the fœtuses. W. D. H.

**Formation of Sugar in Animals.** By MANEO KUMAGAWA and RENTARO MIURA (*Chem. Centr.*, 1899, i, 299; from *His-Engelmann's Archiv. Physiol. Abth.*, 1898, 431—450).—In starving dogs, injection of phloridzin leads to glycosuria, although such animals had no glycogen and but little fat in their bodies; the sugar must arise from proteid. In another animal, which was fat, the same result followed the injection. The amount of sugar stands in constant relation to the amount of proteid metabolism.

W. D. H.

**Formation of Sugar from Proteid.** By RUDOLF COHN (*Zeit. Physiol. Chem.*, 1899, 28, 211—218).—It is known that aspartic acid and glycocine, when given to animals, increase the amount of liver glycogen; the present experiments on rabbits show that the same is true for leucine. Now leucine is the largest product of proteid decomposition (50 per cent. in the case of casein). It is regarded as probable that leucine is the source of sugar from proteid. A comparison of the formulæ of leucine,  $\text{CH}_3 \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{NH}_2) \cdot \text{COOH}$ , and dextrose,  $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH}(\text{OH})]_3 \cdot \text{CH}(\text{OH}) \cdot \text{COH}$  shows this to be by no means impossible. No complicated synthesis is involved; oxidation, splitting off of the amido-group, and reduction are all that are necessary. The fact that leucine leads to glycogen formation lends support to this view.

W. D. H.

**Fibrin Formation.** By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1899, 28, 98—114. Compare Abstr., 1897, ii, 152).—By means of repeated precipitations, fibrinogen was obtained almost free from calcium (0.006 per cent.). Ferment solutions were prepared from oxalated plasma which contained only 0.00004 to 0.0007 per cent. of calcium. On mixing the two solutions, typical fibrin was formed which contained only 0.006 per cent. of calcium, or in some cases even less. Fibrin is therefore not a calcium compound of fibrinogen. The small amount of calcium present must be regarded as an impurity, for if it were in chemical combination the molecular weight of fibrin must be greater than 800,000, or fifty times greater than that of oxyhæmoglobin. Quantitative experiments on the relationship of fibrin and fibrinogen showed that from 63 to 83 per cent. of the fibrinogen appeared as fibrin. In some of these experiments, calcium chloride was added, in others not; the difference in the amount of fibrin formed is always insignificant; if only a small amount of the calcium salt is added, fibrin formation is rather more rapid; if the amount of calcium salt is increased, the amount of fibrin formed is slightly diminished; in other words, it acts like other neutral salts.

The formation of fibrin from fibrinogen is usually regarded as a process of hydrolysis, the fibrinogen splitting into fibrin and fibrinoglobulin. Schmiedeberg's equation (*Arch. exp. Path. Pharm.*, 39) for this would require that only 48—49 per cent. of the fibrinogen should appear as fibrin. The difference between the elementary composition of fibrin, fibrinogen, and fibrinoglobulin is so slight as to suggest that the process is not necessarily one of hydrolysis at all. It may be that it is simply a matter of intramolecular rearrangement, varying quantities of the altered fibrinogen reappear as fibrin, and part remains in solution as fibrinoglobulin. Possibly casein formation is similar.

W. D. H.



**Origin of Fibrinogen.** By ALBERT MATHEWS (*Amer. J. Physiol.*, 1899, 3, 53—85).—The experiments recorded are believed to support the conclusion that the fibrinogen of the blood originates from the decomposing leucocytes, especially of the intestinal area. Fibrinogen increases when the number of leucocytes increases; after removal of the intestine, there is little or no renewal of the fibrinogen if the animal's normal blood has been previously replaced by defibrinated blood. This is not so when organs other than the intestine are removed.

W. D. H.

**Formation of 3-Methylxanthine from Caffeine in the Animal Organism.** By MANFREDI ALBANESE (*Ber.*, 1899, 32, 2280—2282. Compare Abstr., 1896, ii, 319, 492).—The change which caffeine undergoes on passing through the animal organism is somewhat different from that suffered by theobromine, which by dogs and rabbits is transformed into 7-methylxanthine (heteroxanthine). In dogs, caffeine is changed into 3-methylxanthine; in rabbits, into xanthine, and in man into dimethylxanthine, the latter being probably the 1:3-derivative.

J. F. T.

**Glycocine.** By KARL SPIRO (*Zeit. physiol. Chem.*, 1899, 28, 174—189).—Glycocine is obtained among the amido-acids which are decomposition products of many true proteids, and not only from albuminoids like gelatin. If this occurs also in the body, glycocine must be regarded as one of the precursors of urea.

W. D. H.

**The Melanin of the Eyeball.** By HANS LANDOLT (*Zeit. physiol. Chem.*, 1899, 28, 192—210).—The pigment granules of the retina have no stroma; the elementary composition of the pigment is C, 54.56; H, 5.34; N, 12.7; O, 27.4 per cent. The ratio C:N=5:1. By the action of acids and alkalis, the composition changes, the carbon percentage rising, the nitrogen falling. Many previous observers have attempted to separate the pigment by a method involving gastric digestion; this accounts for the higher C:N ratio they have obtained. The end product of the action of boiling with acid, or of fusing with alkali, has a composition in which C:N=13:2. By fusing with alkali, indole, ammonia, and volatile fatty acids are given off. By the action of acid, an aromatic complex giving Millon's reaction is formed. Although there is a probable relation between the pigment and proteid matter, the experiments given do not bear witness to any intimate relationship between the pigment and hæmoglobin or hæmatin.

W. D. H.

**"Crystalline Fibrin."** By S. DZIERZGOWSKI (*Zeit. physiol. Chem.*, 1899, 28, 65—72).—Maillard (this vol., i, 466) has described a crystalline deposit which occurs in phenolised blood serum (ox and horse) when it is allowed to stand; he termed it crystalline fibrin.

The deposit, however, is partly amorphous; and by means of suitable solvents can be separated into four constituents; (1) calcium salts of the higher fatty acids; (2) compounds of these acids with glycerol and cholesterol; (3) proteid matter which is digestible by gastric and pancreatic juices; (4) nuclein. It is the two first upon which the crystalline character of the deposit depends.

W. D. H.

**Uric Acid in Mammals.** By OSKAR MINKOWSKI (*Chem. Centr.*, 1899, i, 212—213; from *Arch. exp. Path. Pharm.*, 41, 375—420).—Uric acid is synthetically formed in the liver of birds; the question investigated is whether mammals have a similar synthesising power. It was found, however, that after administration of large quantities of urea and ammonium sarcosylactate, or allantoin, there is in dogs no rise in the amount of uric acid secreted.

Feeding on calves' thymus or nuclein from the salmon leads to a rise of the uric acid in the urine; but the nuclein bases do not act in this way. W. D. H.

**Uric Acid Infarcts in New Born Children.** By H. SPIEGELBERG (*Chem. Centr.*, 1899, 211—212; from *Arch. exp. Path. Pharm.*, 41, 428—438).—The kidneys of children who die during the first weeks of life, show, as a rule, a deposit of urate crystals, the so-called uric acid infarcts. Experiments on dogs show that the adult organism is able to decompose far more uric acid than the young animal. After subcutaneous injection of uric acid in new-born animals, typical infarcts are formed. This relationship of the young animal to uric acid is something quite special. With other substances, there is no evidence of diminished power of oxidation. W. D. H.

**Xanthine Bases in the Suprarenals.** By JOHANN OKERBLOM (*Zeit. physiol. Chem.*, 1899, 28, 60—64).—From 1·8 kilos. of fresh suprarenals, only 0·5 gram of xanthine bases was obtained; the principal base present is xanthine; then follow 1-methylxanthine, hypoxanthine, epiguanine, and adenine. W. D. H.

**Oxidising Ferment of the Liver.** By MARTIN JACOBY (*Virchow's Archiv*, 1899, 157, 235—280).—The oxidising ferment of the liver resists to some extent the action of alcohol; small quantities of chloroform increase its activity, but in larger quantities of this reagent the activity of the ferment, as tested by the action of the minced organ on salicylaldehyde, is destroyed. The addition of small quantities of alkali furthers, but of larger quantities (beyond 0·3 per cent. of sodium hydroxide) destroys, its activity. Very small quantities of hydrochloric acid do not lessen its action, but when the concentration reaches 0·1 per cent., only traces of salicylaldehyde are oxidised. A temperature of 75° does not completely destroy the ferment, but one of 100° does so. Various substances were subjected to the action of the minced liver in order to see which of them were oxidised; no oxidising action was observed on sodium thiosulphate, sodium acetate, stearic, or palmitic acids. Sugar is not formed from these fatty acids. Uric acid also is not destroyed by calves' liver; but with dogs' liver there is some indication of oxidising action. In diabetes, the oxidising action of the liver is normal. The glycolytic ferment is not identical with the oxidising ferment; the former is destroyed at the comparatively low temperature of 58°, and is differently affected by chemical reagents as compared with the latter. Glycolysis appears to be a function of the cells. The liver is able to oxidise small quantities of arabinose. The change of glycogen into sugar does not appear to be due to the oxidising ferment. Oxidations in

the body fall under three main headings: (1) those which are not fermentative; (2) those brought about by cells; and (3) those produced by oxidases in the body-juices.

W. D. H.

**Thyroid Gland.** By ERNST ROOS (*Zeit. physiol. Chem.*, 1899, 28, 40—59).—A large number of estimations of the iodine in the thyroids of different animals are given. As a rule, this element is more abundant in the vegetable feeders; but it is sometimes absent even among these.

Renewed researches confirm the author's previous statements that the main active substance is iodothyryn. No actual observations are recorded on myxœdema, but other diseased conditions were observed, and experiments made on metabolism.

W. D. H.

**Physiology of the Iodine-containing Substance of the Thyroid Gland.** By F. BLUM (*Pflüger's Archiv*, 1899, 77, 70—106).—Fresh experiments are recorded to confirm the author's previous conclusions (this vol., ii, 115) that the thyroid is an excretory organ removing poisonous substances from the blood, and that the iodine found there originates in this way. Iodothyryn is regarded as an artificial product; the iodine of the thyroid is in combination with proteid; the proteid is not fully saturated with iodine, and the amount of iodine per cent. varies considerably. The proteid itself belongs to the toxalbumins. Ostwald's thyreoglobulin, obtained by half-saturation with ammonium sulphate, is not a single substance. The thyroid gland is not to be regarded as an organ pouring a useful internal secretion into the circulation; the lymph leaving it, and the lymphatic glands in its vicinity do not contain iodine; and the blood and central nervous system in healthy animals are also free from iodine. Removal of the thyroid is followed by disease and death, because the organ which removes poisonous substances from the blood can no longer protect the animal. It is the central nervous system which principally suffers, and by Nissl's method great changes (chromatolysis) can be demonstrated in the ganglion cells. The thyroid therefore appears to be the great protective organ to the central nervous system. The poisonous substances are destroyed by oxidation, and this appears to be assisted by combination with iodine.

W. D. H.

**Coagulating Action of the Liquid of the External Prostate of the Hedgehog on the Contents of the Vesiculæ Seminales.** By L. CAMUS and EUGÈNE GLEY (*Compt. rend.*, 1899, 128, 1417—1419).—The prostatic liquid of several rodents coagulates the contents of their vesiculæ seminales. In the hedgehog, one of the Insectivora, there is a substance of the same order. This animal possesses a gland which appears to be an accessory prostate, and is termed the external prostate; its secretion, which is very alkaline, contains a ferment termed *vesiculase*, which causes a flocculent clot in the secretion (*vesiculin*) of the vesiculæ seminales. Its activity is destroyed at 69°. It does not act on the vesiculin of the guinea-pig, or *vice versa*.

W. D. H.

**Agglutination produced by the Albuminous Gland of Helix Pomatia.** By L. CAMUS (*Compt. rend.*, 1899, 129, 233—234).—An

aqueous or saline extract of the albuminous gland of the snail, *Helix pomatia*, possesses the power of causing agglutination of milk globules and of blood corpuscles.

W. D. H.

**A Substance in the Blood which prevents the Action of Rennet on Milk.** By A. BRIOT (*Compt. rend.*, 1899, 128, 1359—1361). By L. CAMUS and EUGÈNE GLEY (*ibid.*, 1416—1417).—The blood serum of the horse and other animals contains a substance which is capable of neutralising the effects of a certain quantity of rennet. It does not dialyse, is destroyed by heat, and is precipitable by alcohol and by ammonium sulphate. On these grounds, it is believed to be an enzyme. Egg-white has the same power. The anti-rennet action of the serum of an animal can be augmented by repeated injections of rennet subcutaneously.

CAMUS and GLEY point out that they have previously described the anti-rennet action of serum, and that serum also acts counter to pepsin and trypsin.

W. D. H.

**Composition of Cerebro-spinal Fluid.** By GUERBET (*J. Pharm.*, 1899, [vi], 10, 59—61. Compare Abstr., 1898, ii, 36).—The reducing substance present in cerebro-spinal fluid is not precipitated by lead acetate, and its solution is not darkened by alkalis or coloured by ferric chloride. The author concludes that it is not catechol, nor can it be glucose, since its solution is without action on polarised light, and gives no precipitate with phenylhydrazine acetate. Unsuccessful attempts were made to isolate the reducing substance.

H. R. LE S.

**Fate of Cholesterol in the Animal Organism.** By VINCENZ HUMNICKI (*Chem. Centr.*, 1899, i, 369; from *Dissert. Freiburg*, 1898).—In the human body, chloesterol is discharged in the fæces as coprosterol. Particulars are given of the crystalline form, melting point, &c., of compounds of this substance with acetyl, propionyl, benzoyl, and other radicles.

Coprosterol was not obtained by the putrefaction of cholesterol *in vitro*. In dogs, cholesterol is contained in the fæces as such. In horses, a different reduction product, hippocoprosterol, was obtained; but its formula was not determined; it crystallises in short needles, and melts at 74—75°.

W. D. H.

**Excretion of Uric Acid.** By SCHREIBER and WALDVOGEL (*Chem. Centr.*, 1899, i, 849; from *Arch. exp. Path. Pharm.*, 42, 69—82).—Two students fasted for three days. At the beginning of the research, they passed daily 0.477 and 0.718 gram of uric acid respectively, and on the third day 0.197 and 0.205 gram. The amount of uric acid does not run parallel to the total nitrogen or to the acidity of the urine; it does not disappear with vegetable diet. Animal food causes a rise in the xanthine bases, but not in the uric acid excreted, whilst salicylic acid causes a rise in both.

W. D. H.

**Action of Hydrogen Peroxide on Urine. Origin of Acetone.** By S. CORRON (*J. Pharm.*, 1899, [vi], 10, 193—200).—Acetone is present in all animal liquid secretions, and in urine more than in any other; it is also present in the breath. Besides acetone, normal

urine may also contain other ketones which give the iodoform reaction. Acetone is produced from nearly all organic compounds when they are heated with hydrogen peroxide. Citric acid, tartaric acid, glycerol, and the sugars give a large amount of acetone; the oils and fats give a small amount of acetone but much acetaldehyde, and the proteids give a large amount of acetone and benzaldehyde.

H. R. LE S.

**Action of Mineral Substances and Organic Acids on the Resistance of the Body to Disease.** By ALBERT CHARRIN, GUILLEMONAT, and LEVADITI (*Compt. rend.*, 1899, 129, 305—307. **Immunity and Specificity.** By CHARLES BOUCHARD (*ibid.*, 308—311).—During several weeks, rabbits received every day or two subcutaneous injections of increasing quantities of a saline solution containing sodium sulphate, phosphate and chloride, and potassium phosphate. Other rabbits received injections of organic acids like lactic, oxalic, and citric. The diet throughout was constant. Finally, they were inoculated with cultures of *Bacillus pyocyaneus*. The 'acid animals' died more quickly and the 'saline animals' lived much longer than normal animals; *post mortem*, the bone marrow of the saline animals was found to be hypertrophied, and had lost some of its fat.

BOUCHARD points out that these results confirm his theories of immunity.

W. D. H.

**Orthamidophenetidine [Relation of Constitution and Physiological Action].** By GEORG COHN (*Ber.*, 1899, 32, 2239—2243).—See this vol., i, 944.

**Effect of Inorganic Solutions, and Solutions containing Serum-albumin on the Frog's Heart.** By E. C. WALDEN (*Amer. J. Physiol.*, 1899, 3, 123—133).—If a heart is stopped by irrigation with normal saline solution, Ringer's solution sets it going again, and if this brings it, as it will in many hours, to a standstill, increase of the calcium in the fluid once more causes recovery. Blood serum, or milk, has little or no effect in this direction. Experiments with pure serum-albumin show that it has none of the special nutritive value in connection with the heart which has been attributed to it by Kronecker.

W. D. H.

**Behaviour of Salol and Distearyl Salicyl Glyceride in the Organism.** By VINCENZ HUMNICKI (*Chem. Centr.*, 1899, i, 369; from *Dissert. Freiburg*, 1898).—After taking salol, the separation of salicylic acid in the urine occurs more slowly than after taking salicylic acid. Distearyl salicyl glyceride, in contradistinction to trisalicyl glyceride, is almost completely absorbed. The passage of salicylic acid into the urine takes place more slowly after taking salol than after the administration of sodium salicylate.

W. D. H.

**Physiological Action of Choline and Neurine.** By FREDERICK W. MOTT and WILLIAM D. HALLIBURTON (*Proc. Roy. Soc.*, 1899, 65, 91—94; *Phil. Trans.*, 1899, 191, B, 211—267. Compare Abstr., 1897, ii, 222; 1898, ii, 242; this vol., ii, 315).—A full account of a research of which preliminary communications have already been made.

W. D. H.

**Physiological Effects of Extracts of the Pituitary Body.**

By EDWARD ALBERT SCHÄFER and SWALE VINCENT (*J. Physiol.*, 1899, 25, 87—97. Compare this vol., ii, 441).—Extracts of the infundibular (not the hypophysal) part of the pituitary body contain two substances, one of which, when injected intravenously, produces a rise, the other a fall, of blood pressure. The rise is partly of cardiac origin, and is partly due to constriction of the peripheral vessels. After atropine, the rise is enormous; it differs from that produced by suprarenal extract in that a second dose given soon after the first fails to produce any effect. This allows the second substance to have full play, and the fall of blood pressure may be obtained any number of times with successive doses. The subcutaneous injection of the extracts in small mammals causes paralytic symptoms, similar to those obtained by injecting suprarenal extracts.

The characteristic effects produced by extracts of the infundibular body are probably not due to the grey, nervous matter of which it is largely composed. The substance which produces the fall of blood pressure is not choline, although like it at first sight. After a small dose of atropine, the action of the infundibular depressor substance is unaffected, whereas that of choline is abolished, or even a rise of blood pressure produced. The chemical nature of neither of the active substances was made out; they are not destroyed by boiling, and are dialysable; they are not proteid in nature; the depressor substance is soluble in salt solution, in absolute alcohol, and in ether; the pressor substance is soluble in salt solution, but not in absolute alcohol or in ether.

W. D. H.

**The Relation of the Toxin and Anti-Toxin of Snake Venom.**

By CHARLES JAMES MARTIN (*Proc. Roy. Soc.*, 1898—1899, 64, 88—94. Compare this vol., ii, 234).—This is a record of fresh experiments to support the previous conclusions of the author that the reaction of toxin and anti-toxin is a chemical one. About the same quantity of anti-venen necessary to neutralise the venom *in vitro* is capable of doing so when the former is injected into the blood stream and the latter subcutaneously. In fact, the two can be accurately titrated against one another with the life of a rabbit as indicator. Fraser's statement is, however, confirmed that at least ten to twenty times the amount of anti-venen is necessary if both it and the venom are injected subcutaneously. In other words, anti-venen is slowly absorbed from the subcutaneous spaces; this is owing to the large size of its molecules. In snake bite, therefore, the curative serum should be injected intravenously.

W. D. H.

**Echidnase.** By C. PHISALIX (*Compt. rend.*, 1899, 129, 115—117).—

The experiments recorded are considered to show that a ferment (echidnase) in the venom of vipers exercises a digestive action, not only on the tissues of the animals inoculated, but also on the active principle (echidno-toxin) of the venom. This is supposed to be an internal cause of the destruction of the poison, which aids various external forces (oxygen, light, heat, electricity) that act in the same way.

W. D. H.

**Immunity of certain Animals to the Poisonous Action of Eel's Serum.** By L. CAMUS and EUGÈNE GLEY (*Compt. rend.*, 1899, 129, 231—233).—The frog, toad, fowl, pigeon, and other animals resist the toxic action of eel's serum. This is not due to any material in the blood-plasma (*humoral immunity*) but to a special cellular organisation giving to the red corpuscles a specific resistance. This is termed *cytological immunity*.  
W. D. H.

**Phosphorus Poisoning and Phloridzin Diabetes.** By W. E. RAY, T. S. McDERMOTT, and GRAHAM LUSK (*Amer. J. Physiol.*, 1899, 3, 139—155).—In dogs diabetic with phloridzin, phosphorus poisoning does not materially increase the proteid metabolism nor change the excretion of sugar. In dogs poisoned with phosphorus, phloridzin causes the usual sweeping out of the body sugars; then the establishment of the ratio in the urine of dextrose to nitrogen of 3.75 to 1. It causes further an increase of proteid metabolism, and the urine, from being ammoniacal, becomes acid. In one animal, tyrosine crystals were excreted temporarily. The vomit in phloridzin diabetes does not contain sugar. Six minutes after the subcutaneous injection of phloridzin, sugar may be detected in the urine. *Post mortem* after phloridzin diabetes, much fat is found in liver, kidneys, heart muscle, and voluntary muscle. After both phloridzin and phosphorus, the same is found, *plus* fragmentation of the liver nuclei. After phosphorus alone, fat is found in the liver, and in the kidney (slightly), but none in muscle; there is fragmentation of the liver nuclei.

The following general explanation is offered for phloridzin poisoning: the high proteid decomposition is due to the non-burning of the carbohydrate-like radicle of the proteid molecule. In phosphorus poisoning, the high proteid decomposition is due to the conversion of this radicle into leucine, tyrosine, and fat (*fatty degeneration* in Virchow's sense); wherever the sugar from proteid is not burned, pathologically hungry cells are found, which attract fat to themselves in larger quantities than can be utilised (*fatty infiltration*). Infiltration takes place generally in the tissues in phloridzin diabetes; infiltration and degeneration take place in phosphorus poisoning, especially in the liver.  
W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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Artificially increasing the Quantity of Zymase in Yeast. By ROBERT ALBERT (*Ber.*, 1899, 32, 2372—2374).—When yeast, which, under treatment by Buchner and Rapp's method (*Abstr.*, 1898, ii, 127), yields an aqueous extract of feeble activity, is allowed to ferment a solution of cane-sugar, dipotassium phosphate, and magnesium sulphate to which hop-infusion has been added, it is found that the extract subsequently obtained from the yeast



possesses considerably increased fermenting power. An extract prepared from the yeast when most actively fermenting the nutrient solution contains less zymase than at any other time; when the fermentation is complete, the proportion of zymase present is a maximum, and is not increased either by lowering the temperature during nutrition or by leaving the yeast in contact with the nutrient medium for a longer period, although rendered greater by increasing the amount of cane sugar originally present in the latter. W. A. D.

**Variations in the Production of Glycerol in the Alcoholic Fermentation of Sugar.** By J. B. VINCENT LABORDE (*Compt. rend.*, 1899, 129, 344—347).—The fermentation of grape juice by different yeasts yields proportions of glycerol varying from 2·5 to 7·75 per 100 grams of sugar, according to the nature of the yeast, the highest quantity being obtained with Sauterne yeast and with a Martinique yeast from the fermentation of sugar-cane syrup. The feebleness of the activity of the yeast, or the less favourable conditions with respect to active fermentation, the higher the proportion of glycerol formed. An increase in the proportion of sugar increases the proportion of glycerol, and increased acidity has a similar effect. If all the natural acid exceeding 1 per cent. is carefully neutralised, the variations in the proportion of glycerol become very small. Increased temperature promotes the formation of glycerol. With the same sugar and the same yeast, the proportion of glycerol is highest in the early stages of fermentation and diminishes as the change proceeds, because alcohol tends to prevent the formation of glycerol.

The proportion of glycerol is affected by the nature of the sugar as well as by the nature of the yeast, and different sugars may, from this point of view, arrange themselves in different orders with different yeasts.

The high proportion of glycerol found in special wines such as Sauternes is in part due to the action of *Botrytis cinerea* on the must before fermentation. C. H. B.

**Fermentation of Barbary Figs.** By ROLANTS (*Ann. Agron.*, 1899, 25, 395—396; from *Ann. Inst. Pasteur*, 13, 152).—Indian or Barbary figs (*Cactus opuntia*) contain the following amounts of constituents per cent.: water, 84·65; sugar, 10·00; pectic substances, 1·573; extractive substances, 2·614; ash, 1·057. The acidity (as sulphuric acid) is 0·036.

The chief difficulty in utilising figs for obtaining alcohol is the presence of pectic substances, which, however, are rendered insoluble by heating for 20 minutes at 120°. The yield of alcohol is 41 litres from 1000 kilos. of fruit. The alcohol is of good quality and contains aromatic etheric salts of agreeable odour which can be readily removed by rectification. N. H. J. M.

**Acetic Acid Bacteria.** By D. P. HOYER (*Chem. Centr.*, 1899, i, 854; from *Arch. Néerl. Sci.*, [ii], 2, 191—240).—*Bacterium aceti* and *B. xylinum* differ from *B. rancens* and *B. pasteurianum* in their power of inverting sugar. Malic and citric acids and their salts induce fundamental changes in the form of the bacteria of beer vinegar. Acetic acid bacteria live in absence of air, and under this condition reduce

indigotin, methylene-blue, and litmus. The development of the bacteria is accompanied by elimination of carbonic anhydride. As sources of nitrogen, they can utilise peptone, asparagine, nitrites, and ammonium salts, whilst acetic acid, sodium acetate, potassium lactate (and for *B. aceti* and *B. xylinum* also cane-sugar) serve as sources of carbon. The nature of the carbonaceous food determines the assimilability of certain nitrogenous substances, and *vice versa*. A distinction is made between the substances essential for the growth of the cells ("genetic") and others ("zymotic") such as lactic, succinic, malic, and gluconic acids, and calcium lactate, acetate, and propionate. Tartaric acid is not attacked. Less than 4 per cent. of alcohol has no effect on the growth of the bacteria; a larger amount hinders, and about 9 per cent. stops their development. Acetic acid hinders the growth.

N. H. J. M.

**Nitrugin and the Nodules of Leguminous Plants.** By MARIA DAWSON (*Proc. Roy. Soc.*, 1898, 64, 167—168).—The parasitic nature of both the filaments and the bacteroids in root nodules is confirmed. The infection tubes and the filaments in the cells consist of straight rodlets imbedded in a colourless matrix which does not consist of cellulose, chitin, or any form of slime. When the rodlets are liberated by the bursting of the filaments, they become transformed into X-, V-, and Y-shaped bacteroids. This change of form does not occur outside the plant on solid media, but takes place in liquid pea extract. It is uncertain whether the change in form is due to branching or to fusion of two or more individuals. Their multiplication by division would indicate that the organisms are members of the *Schizomycetes*. The bacteroids seem to be incapable of further growth. They are aerobic.

Nitrugin consists of minute, micrococcus-like bodies all straight and immobile. Crossing of kinds supplied for different genera and species is successful within the tribe of *Viciace*. Infection of quite young radicles is tolerably certain, and of older roots when the condition under which they germinated is maintained. The accumulation of carbonic anhydride round the roots is not the cause of failure in direct infection.

Application of nitrugin to soils rich in nitrates seems to be inadvisable; when nitrates are deficient, its application results in an increased yield, but the addition of nitrates instead of nitrugin gives still better results.

N. H. J. M.

**Respiration of Mould Fungi in different Nutritive Solutions.** By KONSTANTIN A. PURIEWITSCH (*Chem. Centr.*, 1899, i, 1251, from *Ber. deut. botan. Ges.*, 16, 290, and *Centr. Bakt. Par.* [ii], 5, 223—224).—The results of experiments in which *Aspergillus niger* was cultivated in solutions containing dextrose, saccharose, mannitol, and tartaric acid showed that the quotient  $\text{CO}_2/\text{O}_2$  rises with the concentration of the solution up to a certain point, and then falls again.

N. H. J. M.

**Action of some Poisons on Yeast and on Fermentation.** By CARL WEHMER (*Chem. Zeit.*, 1899, 23, 163—165).—The want of agree-

ment in the results of experiments hitherto made on the effect of poisons on yeast is attributed to the amount of yeast employed not being taken sufficiently into account. In the experiments now described, the amounts of yeast were the same in each case, and also the amounts of wort.

With 5 grams of yeast and 50 c.c. of wort, 1 gram of potassium and sodium arsenite had in 80 hours no effect, whilst formalin (0.5 c.c. = 0.2 c.c. formaldehyde), chloroform (0.5 c.c.), mercuric chloride (0.25 gram), and benzoic acid (0.5 gram) almost completely checked fermentation. Even 10 per cent. of potassium arsenite did not entirely suppress fermentation. In absence of yeast, or with very little yeast, 1—2 per cent. of arsenite will prevent decomposition of wort for months.

Yeast which has ceased to be active after addition of arsenites, &c., is not necessarily dead. Alkali arsenites (1—2 per cent.) generally destroy yeast after 2—3 weeks, but had no appreciable effect in 3—4 days; with mercuric chloride (0.1—0.25 gram in 100 c.c.), most of the yeast cells were alive after 3 days, but were all killed in 5 days. Benzoic acid, which at once checked fermentation, required more than 1—2 weeks to destroy the yeast, whilst chloroform proved to be the least destructive.

N. H. J. M.

**Chemical Physiology of Ethereal Oils.** By THOMAS BOKORNY (*Chem. Zeit.*, 1899, 23, 60—61 and 75—76. Compare this vol., ii, 318).—Although ethereal oils probably play no part in plant assimilation, the author suggests that their function may be that of antiseptics. The action of the following substances, which occur in various ethereal oils on different minute organisms such as bacteria, moulds, &c., has been studied, and, with the single exception of saligenin, all have proved to have antiseptic properties. Eugenol, cinnamaldehyde, vanillin, salicylaldehyde, saligenin, benzaldehyde, piperonal, coumarin, borneol, carvacrol, thymol, oil of lavender, oil of turpentine, menthol, carvene, carvol.

Most of the substances were employed in 0.1 per cent. aqueous solution.

J. J. S.

**Antiseptic Action of Salicylaldehyde and Benzoic Anhydride.** By ERNST SALKOWSKI (*Virchow's Archiv*, 1899, 157, 416—424).—Bokorny has recently (this vol., ii, 318) called attention to the poisonous action of salicylaldehyde on fungi. The author has already pointed out the antiseptic action of this substance and of benzoic anhydride (*Centr. med. Wiss.*, 1887, No. 51); he now presents experiments which illustrate this action.

W. D. H.

**Action of Enzymes and Substances which kill Bacteria.** By SACHAROFF (*Chem. Centr.*, 1899, i, 941—942; from *Centr. Bakt., Par.*, [i], 25, 346—350).—Iron nuclein can be separated from papayotin more readily by water and hydrogen peroxide than by water alone, and the filtrate is almost free from iron. Addition of ammonium or hydrogen sulphide to the liquid again induces the property of dissolving gelatin, owing, probably, to the presence of traces of iron-nuclein remaining even after repeated filtration. The checking of the

dissolving action of papayotin is attributed, not to its destruction, but to the presence of hydrogen peroxide.

Oxidation in dead or living organisms and in blood is due to the presence of enzymes, and the iron-nuclein present in cell-protoplasm. Active iron-nucleins, the author terms bionucleins.

The author assumes that a bionuclein is present in diphtheria toxin. Toxoids (Ehrlich, *Deut. Med. Woch.*, 24) are probably toxins which have lost their bionuclein through oxidation. N. H. J. M.

**Mutual Relations of the Decompositions of Albumin and of Respiration.** By DMITRI N. PRIANISCHNIKOFF (*Landw. Versuchsstat.*, 1899, 52, 137—164. Compare *Abstr.*, 1896, ii, 380).—Experiments on the germination of peas, lupins, and vetches in the dark showed that the maximum decomposition of proteids and the maximum production of asparagine took place at nearly the same period (about the 7th to 9th day), and some days earlier than the maximum elimination of carbonic anhydride. At the conclusion of the germinating period, the energy of accumulation of asparagine became greater than the rate of decomposition of proteids, asparagine being then produced from amido-acids, if the possibility of its production from newly-formed proteids (at a period when the conditions are favourable to destruction rather than formation of proteids) is not admitted. This involves the breaking up of two mols. of amido-acid, one of which must be oxidised in order to furnish the  $\text{NH}_2$ -group, the other only sufficiently oxidised to yield aspartic acid.

Whilst, according to Loew and Palladin, the decomposition of proteids is a process of oxidation, and according to E. Schulze a process of hydration, the author considers that both processes are successively involved: first a hydration of the proteid molecule, and subsequently oxidation with production of ammonia and also asparagine. This would be analogous to what takes place in the animal organism.

N. H. J. M.

**Progress of Assimilation in Oats in the Field and in Pots.** By ADAM KARPINSKI (*Bied. Centr.*, 1899, 28, 546—550; from *Zeit. landw. Versuchswesen Österr.*, 1898, i, 387).—Field experiments with oats were made at Dublany, in which four plots received (1) no manure, (2) Chili saltpetre, (3) Chili saltpetre applied at two different periods, and (4) ammonium sulphate. A similar set of experiments was made with the same soil in pots. Samples of the plants from both sets were taken at four successive periods of growth.

The results of the two series of experiments differed in several respects. The pot plants contained about half as much nitrogen again as those grown in the field, and were in every respect more strongly developed. This difference is attributed to the difference in the amounts of water at the disposal of the two sets of plants, and to the fact that there was no loss of soluble manure in the pots through leaching.

In the field, ammonium sulphate proved to be better than the nitrate, whilst in pots the nitrate was more effective. Phosphoric acid was taken up chiefly in the first two periods in the field experi-

ments, whilst in the pots it was taken up in the third and fourth periods, although to a less extent than in the first and second.

The roots of both field and pot plants were found to be rich in nitrogen and phosphoric acid during the first period of growth. The roots of the pot plants were much richer in these constituents than those of the field plants, owing, perhaps, to the greater amount of water in the soil of the pots.

N. H. J. M.

**Influence of Light on the Growth of Clover.** By AIMÉ PAGNOUL (*Ann. Agron.*, 1899, 25, 353—356).—Incarnate clover was grown in pots, one pot being exposed to strong light, whilst the other was shaded. Under the influence of strong light, the growth was normal, but the plants screened from direct light developed very badly. The evaporation from both pots was determined during the whole period of growth (May 1 to June 7). At the conclusion, the following results were obtained :

	Evaporation. c.c.	Fresh produce. Grams.	Dry produce. Grams.	Nitric N. in dry produce. Per cent.
1. Plants in strong light.....	3475	31·68	6·23	0·0
2. „ shade .....	1715	4·54	0·40	0·001125

There was thus an accommodation of nitrates in the shaded plants which the plants were unable to reduce. At an earlier stage (May 11), the plants exposed to full light contained a small amount of nitric nitrogen (0·000035 per cent.), but this was completely used up during the next month.

N. H. J. M.

**Forms and Conditions under which Chlorine is usually taken up by Plants.** By P. PICHARD (*Compt. rend.*, 1899, 128, 615—617).—In most soils, chlorine is present in the form of sodium chloride, but in some calcareous and magnesia soils, which are common in Algeria, calcium and magnesium chlorides occur. The drainage from such soils is alkaline and contains sodium carbonate (*ibid.*, 1876).

Experiments are described in which tobacco was grown in artificial and in natural soils containing varying amounts of chlorides, in addition to nitrates ; more or less potash was present in most cases. All the plants were found to contain some chlorine, and when the soil contained only a little sodium chloride, the whole of the chlorine was absorbed by the plants. Generally, the proportion of chlorine in the plants increases in the relation to the amount in the soil under conditions otherwise equal. Most, if not all, of the chlorine in the plants was in the form of potassium chloride ; an increase in the amount of potash in the soil induces increased absorption of chlorine by the plants. Tobacco leaves may contain as much as 11·23 per cent. of potassium chloride.

Sodium chloride occurs only exceptionally in tobacco, and only when the soil contains as much as 0·1 per cent. ; the sodium in tobacco occurs only in the form of chloride. It is concluded that, in contact with roots, sodium chloride decomposes potassium salts, with production of potassium chloride, which is retained by the plants, whilst the newly-formed sodium salts are returned to the soil.

It was previously shown that the nitric acid of the soil has a very

marked tendency to penetrate into the tobacco plant as potassium salt, and to utilise potassium originally present in very insoluble forms, such as clay and various silicates (Abstr., 1895, ii, 60). The presence of chlorides in soil, and their tendency to be absorbed by plants, is antagonistic to the taking up of nitrates; and it is only owing to their predominance in the soil that nitrates can be absorbed. Diminution of the amount of nitrates in soil gives rise to increased absorption of chlorides.

N. H. J. M.

**The Rôle of Sodium in Plants.** By M. STAHL-SCHRÖDER (*Chem. Centr.*, 1899, ii, 693; from *J. Landw.*, 47, 49—84).—The results of field and pot experiments with oats showed that in presence of plenty of potassium, sodium is only taken up largely when in combination with some acid of which the plant requires considerable amounts, such as phosphoric and nitric acids. In accordance with Contejean's and Guitteau's results, it was found that the sodium remained mainly in the lower parts of the plants. Oats can assimilate large amounts of sodium without injury.

Further experiments with peas, oats, carrots, and buckwheat showed that sodium cannot replace the potassium necessary for the production of the organic matter of plants. The alleged economising of potash manures by soda is attributed to indirect action, only observed in the case of soils which contain plant food in sparingly soluble forms.

N. H. J. M.

**Physiological Functions of Calcium Salts.** By OSCAR LOEW (*Bied. Centr.*, 1899, 28, 541—542; from *Bot. Centr.*, 1898, 74, 257—265).—Calcium salts assist in the organisation of the cell-nucleus and chlorophyll substances by forming compounds of calcium with proteids. Whilst strontium salts are injurious to plants in absence of lime, a sufficient quantity of lime renders strontium almost harmless; analogous results were obtained with magnesium salts in the place of strontium salts. It is concluded that in absence of sufficient lime, the partial exchange of strontium or magnesium for calcium in the calcium-nuclein compounds of the nucleus results in local structural disturbances. If the functions of calcium were merely connected with metabolism, strontium might be expected to perform such functions equally well. The view that calcium is mainly of importance in precipitating oxalic acid is opposed to the fact that certain plants which require much lime are as free from oxalic acids as some other plants which require less lime. The importance of lime for chlorophyll substances is indicated by the fact that leaves are the organs which contain the most lime, that etiolated leaves contain less lime than green ones, and that the whole leaf suffers in absence of a sufficient supply of lime (compare Abstr., 1896, ii, 446).

N. H. J. M.

**Spontaneous Asphyxia and Production of Alcohol in the Deep Tissues of Woody Stems growing under Normal Conditions.** By HENRI DEVAUX (*Compt. rend.*, 1899, 128, 1346—1349).—The internal atmosphere of woody stems frequently contains less

than 10 per cent. of oxygen, whilst that of the deeper tissues must contain still less. On increasing the respiration by keeping stems at 35° for 3 days, the percentage amount of oxygen in the internal atmosphere was greatly reduced, in one case to as little as 0.22 per cent., in four cases to much less than 1 per cent., whilst with two other stems the amounts were reduced from 16.32 and 13.12 to 8.62 and 4.04 respectively.

The respiratory coefficient,  $\text{CO}_2/\text{O}_2$ , is usually constant and less than unity. In these experiments, with increased respiration, this coefficient was, with one exception, greater than unity, and in some cases much greater. These results indicate decomposition of the sugar of the living cells, and it was found that alcohol is, in fact, produced, both at the ordinary temperature and to a greater extent at 35°.

N. H. J. M.

**Formation, Storage, and Depletion of Carbohydrates in Monocotyledons.** By JOHN PARKIN (*Proc. Roy. Soc.*, 1898, 64, 122—123).—The investigation of about 70 species, belonging to the principal groups of monocotyledons, showed that the amount of starch, due to normal assimilation in the leaves, varies considerably in different genera. Relatively few produce much, and some none, but species from most of the principal families form some starch in their mesophyll.

On comparing the type of leaf, its position and age, some connection seems to exist with the storage or non-storage of temporary starch; broad leaves, those of aquatic monocotyledons and those working at higher temperatures in the summer, seem more liable to have starch than narrow radical leaves, leaves in dry situations and those of spring species. It was found that starch is developed in the young leaves of *Allium*, a genus long known not to form starch under ordinary conditions, so that the age of the leaf would also seem to affect the question.

Cane sugar was found to produce starch far better than any other sugar in pieces of leaves floated on the solution, invert sugar, glucose, and fructose following next in order, whilst maltose is almost useless.

Inulin is by no means uncommon in monocotyledons, and may coexist with starch in the same cell. It is not stored in aquatic species. Whilst ordinary inulin from *Helianthus* and other *Compositæ* dissolves at about 50°, inulin from *Scilla* dissolves readily in cold water, and inulin from *Galanthus* requires water at 80° for solution.

N. H. J. M.

**Darkening of Sugar Beet Juice.** By MAX GONNERMANN (*Chem. Zeit.*, 1899, 23, 213—215 and 240—242).—Albuminous compounds present in sugar beet are converted by the catalytic action of enzymes into tyrosine, and subsequently into dihydroxyphenylacetic acid, a substance which, when exposed to air, acquires a cherry-red colour or becomes black. No coloration takes place in absence of oxygen or in presence of mineral acids. Slight alkalinity at once produces the coloration.

The process takes place to a slight extent in leaf stems and in the roots; in cut roots and expressed juice, the rate of darkening increases as access of air is increased.

Dihydroxyphenylacetic acid can be detected after keeping fresh beet-root juice for a week in an atmosphere of hydrogen.

N. H. J. M.

**Root Excretions.** By RUDOLF KOHN (*Landw. Versuchs.-Stat.*, 1899, 52, 315—326).—On inserting acid roots in one arm (A) of a U-tube containing very dilute red litmus solution, it was found that the litmus in the other arm (B) soon became blue. The alkalinity could also be observed with very sensitive litmus paper when water alone, or water containing neutral manures, was employed. The action was more rapid in direct sunlight than in diffused light. In some cases, it was found possible by removing the root from (A) to (B) to reverse the colours. With some plants, the red colour in the arm containing the root extended to the end of the other arm. Plants with very slightly acid roots produced little or no alkalinity. Weeds were found to be more suitable than cultivated plants, as the latter generally died quickly.

The results are attributed to electrochemical action; and attention is called to the fact that roots, like electrodes, are able to withdraw the last traces of dissolved substances.

N. H. J. M.

**Production of Sugar in Beet.** By MAX GONNERMANN (*Bied. Centr.*, 1899, 28, 550—554; from *Bl. Zuckerrübenbau*, No. 20, 309, No. 21, 327).—The seeds of sugar beet do not contain saccharose; the first product of the decomposition of starch seems to be amidulin, after which monosaccharides are produced. The seeds contain an enzyme which is not diastatic. In leaves of eight day plants, neither saccharose nor amidulin could be detected, and the presence of starch was doubtful.

New leaves from old roots contained an inverting enzyme, but the extract had no diastatic effect on starch. Neither the roots nor the new growth of leaves contained lævulose.

Leaves of winter rye contain amidulin and glucose, but no starch. Young leaves of summer rye contain saccharose, but no amidulin, starch, or reducing sugar; the roots contain saccharose, but no amidulin, indicating that the starch is rapidly converted directly into saccharose by a ferment (which was isolated) in the seeds. Diastase is present in undeveloped barley grain. It is concluded that, speaking generally, all seeds contain ferments to decompose the starch, and that amidulin is first formed, and then glucose.

Sugar beet plants 14 days old contained a small amount of sugar in the roots; the leaves contained both an inverting and a diastatic enzyme, to which the production of amidulin in the leaves, and sugar in the roots are due. At a later stage, when the plant had eight leaves, the roots contained only saccharose, and no dextrose or starch; the leaves contained saccharose and reducing sugar, but no amidulin, and starch was only present on the upper sides of the leaves.

Bertrand's tyrosinase is one of the enzymes present in beet leaves and stems. The enzymes produce on the one hand the conversion of starch into amidulin, glucose, and saccharose, and, on the other hand, are the cause of the darkening of fresh beet juice.

It is proposed to designate the beet ferments, which differ from



invertin of yeast, and the diastase of barley, beet-invertase, and beet diastase respectively. The author considers that he has established that sugar is only produced in beet by the intervention of enzymes.

N. H. J. M.

**Physiological Importance of Furfuroids in Sugar Beet.** By JULIUS STOKLASA (*Chem. Centr.*, 1899, i, 890; from *Zeit. Zucker-Ind. Böhm.*, 23, 291—294).—The testa of sugar beet seed is very rich, the pure seeds poor, in furfuroids. During growth, there is a considerable increase in the amount of furfuroids in the seedlings. In the leaves of 10-day old plants, 66.9 per cent., and in the roots 19.6 per cent., of the furfuroids are soluble in water; after 120 days, 39.84 per cent. in the leaves and 14.1 per cent. in the roots dissolve in water, whilst at the end of the vegetating period the dry substance of the leaves yielded 5.88 per cent. of furfuraldehyde, of which the aqueous extract yielded only 0.92 per cent.

Manuring with excessive amounts of nitrate increases the amount of furfuroids and diminishes the production of sugar. Large amounts of soluble phosphates and potassium chloride have the same effect. The result with potassium chloride is in accordance with the fact that chlorine energetically induces the transformation of sugar and promotes the production of hemicelluloses and celluloses. Soil free from lime produced plants containing a smaller amount of substances yielding furfuraldehyde than lime soils.

The dry matter of sugar beet roots, in the first year, contained: hemicelluloses, 14.48; celluloses, 5.22; lignin, 5.03; and yielded 6.3 per cent. of furfuraldehyde. In the second year, the amounts were 11.66, 15.23, 29.84, and 9.02 per cent. respectively. In the first year, most of the pentosans are in the form of hemicelluloses, in the second year they increase in the cellulose groups, and especially in the lignin substances.

N. H. J. M.

**Chlorophylls and the Chlorophylls of Ferns.** By ALEXANDRE ÉTARD (*Ann. Agron.*, 1899, 25, 393—394; from *Ann. Inst. Pasteur*, 13, 456. Compare this vol., i, 381).—Several different chlorophylls may exist in the same plant, and the total number of chlorophylls is greater than the number of different species of plants. Although these substances do not seem to take part in the first stages of growth, it is probable that a trace of the matter which produces them exists among the latent functions of the germ.

As regards the theory that chlorophyll produces formaldehyde from the elements of carbonic anhydride and water, it is pointed out that the fatty or waxy character of chlorophyll is inconsistent with this property; and it is further suggested that all the elements usually found in plants are concerned in the synthesis. Hoppe-Seyler, Gautier and the author have always found associated with chlorophyll a certain amount of mineral matter which, it is suggested, may have a rôle analogous to that of manganese in the biological process of oxidation (compare Bertrand, *Abstr.*, 1898, ii, 128).

The following substances were isolated from ferns (*Aspidium filix femina*): an alcohol,  $C_{16}H_{32}O$ ; carotene, and three *aspidiophylls*,

having the formulæ  $C_{208}H_{347}O_{32}N$ ,  $C_{240}H_{320}O_{31}N_2$ , and  $C_{211}H_{346}O_{48}N_{20}$  respectively.  
N. H. J. M.

**A Proteid Compound of Arginine.** By U. SUSUKI (*Chem. Zeit.*, 1899, 23, 658).—According to Loew, the greater quantity of the arginine obtained from the seeds of conifers exists ready formed, but in a loose combination with the proteid material. The author supports this view, as he finds that the proteids from various Japanese conifers yield small quantities of amido-acids when boiled for some hours with 0.5 per cent. hydrochloric acid; in some cases,  $\frac{2}{3}$  of the arginine appears to be thus loosely combined.  
J. J. S.

**Peptonising Enzyme (Peptase) in Malt.** Separation of Nitrogenous Constituents of Malt, Wort, and Beer. By BOLESŁAW DE VERBNO LASZCZYŃSKI (*Chem. Centr.*, 1899, i, 698—699, 852—853, and 939—940; from *Zeit. ges. Brauw.*, 22, 71—73, 83—86, 123—129, and 140—143).—Barley seedlings, beginning to become green, had no enzymic action on fibrin (compare Neumeister, *Abstr.*, 1895, ii, 290), but green and dark kiln-dried malt showed a distinct action. In no case, however, was there any action in 6 hours at  $40^\circ$ , whilst addition of 10 milligrams of pepsin acts at once.

Malt, wort, and beer do not contain peptone, and the solubility of nitrogenous substances in malt depends on the conditions of extraction. The nitrogen compounds are (1) coagulable proteids, (2) albumoses, and (3) amides. The first are only completely separated by heating for 1 hour at  $1\frac{1}{2}$  atmospheres pressure, and are also precipitated by phosphotungstic acid and copper hydroxide. The latter, however, only partially precipitates those substances which can be separated by zinc sulphate. Copper sulphate precipitates a portion of the albumoses and amides. Phosphotungstic acid separates albumoses, xanthine bases, and a part of the amides.

Sodium hydrogen sulphate and copper sulphate precipitate the xanthine bases in malt extract, &c., but the proteids and albumoses must be first separated, as they are also precipitated.

Uranium acetate does not precipitate all the substances separated by phosphotungstic acid. The latter precipitates almost the same amount of nitrogen as copper hydroxide, but the nitrogen is in part in different forms in the two precipitates. The author rejects both agents and employs the following process. The malt extract is first heated with steam for 1 hour under  $1\frac{1}{2}$  atmospheres pressure, the filtrate precipitated with zinc sulphate, and a little sulphuric acid. After filtering from the albumoses, the xanthine bases are separated by means of sodium hydrogen sulphate, copper sulphate, and barium chloride. The difference between the total nitrogen and nitrogen in the various precipitates gives the amidic nitrogen.

The coagulated proteids include the substances which settle when pasteurised beer is kept, and the less nitrogen beer contains in this form the more suited is it for pasteurisation and keeping. Beer contains 0.01 per cent. of xanthine bases.  
N. H. J. M.

[Ash of] Cardamoms. By H. B. YARDLEY (*Chem. News*, 1899, 79, 122).—Cardamom seeds and husks have been found to yield

4.19 per cent. of ash, of a grey colour, containing per cent. :  $\text{CaO}$ , 13.33;  $\text{Fe}_2\text{O}_3$ , 0.51;  $\text{Al}_2\text{O}_3$ , 1.53;  $\text{MgO}$ , 4.52;  $\text{Na}_2\text{O}$ , 20.43;  $\text{K}_2\text{O}$ , 10.42;  $\text{P}_2\text{O}_5$ , 6.00;  $\text{SO}_3$ , 12.66;  $\text{Cl}$ , 2.54;  $\text{SiO}_2$ , 24.81;  $\text{CO}_2$ ,  $\text{C}$ , &c., 4.40.

HERBERT BRIDGES (*ibid.*, 154) and W. WATSON WILL (*ibid.*, 167) call attention to the presence of manganese in the ash. The latter has found in undoubted specimens of *Elettaria cardamomum* the ash (1) of the whole seeds to be 3.26, crushed 3.52; (2) of the pericarp of fruit, 5.96 and 6.17; of the entire fruit and seeds, 3.8 and 4.219 per cent.

D. A. L.

Coffee. By L. A. WARNIER (*Rec. Trav. Chim.*, 1899, 18, 351—357).

—The paper contains details of the complete proximate analysis of two types of Java coffee, *Coffea arabica* and *C. liberica*; the results are given in tabular form. The aqueous extract of coffee amounts to 30 per cent. of the whole; the quantity of free acid is very variable and diminishes rapidly when the berries are kept for a long time. Coffee berries contain about 15 per cent. of fatty substances,  $1\frac{1}{4}$  per cent. of caffeine, and 4 per cent. of ash; the latter contains 75 per cent. of potash and 10 per cent. of phosphoric acid.

G. T. M.

Composition of the Water-chesnut (*Trapa Natans*). By PAUL NEUMANN (*Chem. Zeit.*, 1899, 23, 22—23, 38—39).—The shells yielded 3.15 per cent. of ash, the composition of which is given; it is characterised by a high percentage of lime, magnesia, and potash, and by an unusual amount of iron and manganese. The composition of the fruit was as follows: water, 10.41; ash, 2.78; fat, 0.73; cellulose, 1.38; crude proteids, 19.93; dextrose, 3.22; starch, 52.19; other nitrogen-free substances, 9.36 per cent. A full analysis of the ash of the fruit is given; this differs from that of the shells by containing more phosphoric acid and potash.

L. DE K.

Action of Acetic Acid Vapour, and Dilute Acetic Acid on Plants. By G. FASSBENDER and A. Y. GREVILLIUS (*Landw. Versuchs-Stat.*, 1899, 52, 195—208).—Young oat plants were destroyed by being kept 4 hours in air containing 0.3—0.4 per cent. of acetic acid. Peas resisted the action of the acid better, whilst beans were only locally and temporarily affected by 0.5 per cent. of acid. Peas were killed by frequently watering the leaves with 0.05 per cent. acetic acid; beans were only injured by 0.5 per cent. acid, and the injury was mainly confined to portions to which drops of the acid adhered.

Water containing 0.001—0.01 per cent. of acid promoted the germinating energy of beans and peas, but the effect was less in the case of flax; no effect was observed with rye. Stronger solutions hindered germination (0.1 per cent. with flax, 0.2 per cent. with beans, peas, and rye). The germinating power of flax was influenced by 0.05 per cent. acid; with peas and rye, the percentage of seeds which germinated was only diminished by 0.2 per cent. acid. None of the seeds germinated in 0.5 per cent. solutions.

The growth of seedlings of peas and beans was promoted by dilute solutions (to 0.01 per cent.).

The points of the roots of seedlings are the parts most readily injured by acid.

N. H. J. M.

**Phosphoric Acid and Cereals.** By CH. GUFFROY (*Bied. Centr.*, 1899, 28, 573—574; from *J. Agric. prat.*, 1898, 62, ii, 52).—Experiments were made with wheat and barley on poor soil (unmanured for at least 15 years). Phosphoric acid was applied in the form of basic slag (500 kilos. per hectare).

The effect of phosphoric acid was to increase the length, thickness, and strength of the straw, whilst the ears were better developed and the sp. gr. of the grain was increased. N. H. J. M.

**Potash Requirements of Brewery Barley.** By THEODOR RÉMY (*Ann. Agron.*, 1899, 25, 397—398; from *Untersuch. Kalibedürf. d. Gerste. Berlin*, 1898).—The results of laboratory and field experiments made by the Berlin Institute of Brewing showed that potash is only effective in the case of soils poor in potash, that climatic conditions, especially the distribution of water, are of great importance, and that it is necessary, by careful tillage, to enable the soil to derive benefit from the manures. Under favourable conditions, the effect of potash is to increase the crop and the amount of starch, to diminish the amount of proteids, and to increase the weight of grain.

In accordance with Liebscher's observations, the lowest limit of potash soluble in 25 per cent. hydrochloric acid which a soil should contain is fixed at 0.15 per cent. Soils containing less than this amount will be benefited by manuring with potash. Application of potash to richer soils is to be avoided, as it increases the demand for other constituents without any benefit to the crop. N. H. J. M.

**Valuation of Meadow Hay.** By WOLDEMAR VON KNIERIEM, (*Bied. Centr.*, 1899, 28, 526—527; from *Landw. Jahrb.*, 1898, Heft. 3—4).—Digestion experiments with rabbits gave the following results with different plants (percentage amounts digested):

	Crude protein.	Crude fat.	Crude fibre.	Non- nitrogenous substances.
White clover .....	68.2	50.9	57.35	83.07
Red clover .....	64.4	75.3	26.46	68.16
Kidney vetch .....	65.8	60.1	27.08	73.53
Vetch .....	71.27	58.03	29.87	69.23
Couch grass (luxuriant) ...	76.01	64.48	15.22	58.47
„ (poor) .....	71.79	63.06	12.37	59.40

Experiments with *Lotus corniculatus* and bastard clover failed, whilst *Lolium perenne* and *Phleum pratense* caused the rabbits to die at the conclusion of the experiment.

As regards the effect of sour hay on milk production, it was found that feeding with sour hay after clover hay at once caused a diminished production of milk, whilst a return to clover hay again raised the yield. Cows utilise sour hay better than sheep. N. H. J. M.

**Tobacco Plant.** By JOHANNES BEHRENS (*Landw. Versuchs.-Stat.*, 1899, 52, 213—246. Compare Abstr., 1895, ii, 524).—The toughness and pliability of tobacco leaves cannot be due, as is frequently assumed, to the presence of substances allied to india-rubber or gum, as these

cannot be detected in the leaves. The chief differences in composition between pliable and "dead" or brittle leaves are in the percentages of water and of substances soluble in water, both of which are higher in well-developed leaves. The composition of the soluble matter also differs, the amount of organic salts (mainly malate) being much higher in normal than in "dead" leaves; the normal leaves were found besides to contain more wax than brittle ones, and it is perhaps to this that their gloss is due. It was found that brittleness could be induced by covering portions of leaves with tinfoil. This is, however, only one cause of defective leaves; excessive manuring with Chili saltpetre produces leaves with lower percentages of soluble matter.

The liability to decay of tobacco from plants manured with nitrate and other soluble manures is attributed to the fact that the leaves take longer to dry, and to the danger of the drying process being stopped before the minimum amount of water required by the putrefying bacteria is reached. The leaves contain, moreover, more nutritive matter suitable for the bacteria than leaves of plants which have received no nitrate.

N. H. J. M.

**Importance of Chemical Analysis in Estimating the Value of Hops.** By THEODOR RÉMY (*Bied. Centr.*, 1899, 28, 563—568; from *Woch. Brauerei*, 1898, Nos. 41—43).—The chemical analysis of hops is not in itself sufficient for estimating their value, but may furnish useful information on a number of points. The amount of resin in hops is determined by extracting the ethereal extract with alcohol, evaporating carefully, and drying the residue at 60° under 1/10th atmospheric pressure. The results of a number of analyses showed that whilst samples of good quality contained 18·5—22·8 per cent. of resin in the dry matter, inferior samples contained only 14·0—17·4 per cent. The percentage of resin does not seem to vary much in hops from different districts.

The portion of the resin soluble in light petroleum (soft resin) is, according to Hayduck, Briant, and Meacham, the substance to which the preserving and bitter qualities of hops are due. Determinations of soft resin in hops from different districts gave results varying from 9·5—17·0 per cent. in dry matter. The amount of soft resin depends, not only on the amount of total resin, but is influenced by the methods of drying, storing, &c.

The determination of tannin in hops seems to be of little use in estimating the value of hops, whilst the total nitrogen and the soluble nitrogen give no indications at all.

The amounts of potash and phosphoric acid in hops were found to be 1·85—3·75 and 1·02—1·63 per cent. in the dry matter respectively.

N. H. J. M.

**Linseed in its Botanical, Chemical, and Agricultural Relations.** By AL. HERZOG (*Bied. Centr.*, 1899, 28, 544—545; from *Publ. Versuchs-Stat., Flachsbaum Trautenau*, No. 3).—Linseed contains, on the average, water, 7·5; crude protein, 23; crude fat, 35; nitrogen-free extract, 22·2; crude fibre, 8·8, and ash, 3·5 per cent. The pure ash contains  $K_2O$ , 28·41;  $MgO$ , 13; and  $P_2O_5$ , 44 per cent.

During the growth of the plant oil migrates from the leaves to the seeds, where it is first transformed into starch. Subsequently (chiefly between the periods of flowering and ripening) the starch is transformed again into oil. According to Schischkin, the amount of oil in the seeds is influenced by manuring.

N. H. J. M.

**Composition of Walnut-cake.** By B. FALLOT (*Bied. Centr.*, 1899, 28, 531—532; from *J. d'agric. prat.*, 1898, 628).—The percentage composition of walnut-cake prepared by the cold (1) and by the hot processes (2—4) was found to be as follows:

	Water.	Proteids.	Fat.	N.-free extract.	Crude fibre.	Ash.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .
1. Cold process	9.40	31.79	27.17	20.61	6.83	4.20	0.87	1.77
2. Hot „ (max.)	15.04	44.87	20.06	33.62	9.01	5.27	1.59	2.40
3. „ „ (min.)	4.11	29.29	9.26	21.96	3.11	4.36	1.27	0.40
4. „ „ (av.)	11.40	37.77	13.68	27.75	4.56	4.77	1.39	1.71

As a concentrated food only to be used in conjunction with other foods, the composition of walnut-cake is very favourable. The following ration for cows was found to be very suitable; walnut-cake (1.5), green maize (15.0), sugar beet (15.0), and oat, chaff, and straw (5 kilograms).

N. H. J. M.

**Experiments on Rape.** By WILHELM GRASHOF (*Chem. Centr.*, 1899, i, 858; from *J. Landw.*, 47, 85—90).—The experiments were conducted in large zinc cylinders filled with soils of different kinds and differently manured. Both the nature of the soil and of the manure influenced the amount of oil in the produce. Phosphatic manure increased the percentage of oil rather more than 2 per cent. When the percentage of oil in rape is high, the nitrogen is low, whilst with a high percentage of nitrogen there is less oil.

N. H. J. M.

**Volatile Mustard Oils [Thiocarbimides] in different Rape Cakes.** By GUNNER JÖRGENSEN (*Landw. Versuchs-Stat.*, 1899, 52, 269—290. Compare this vol., ii, 46).—The seeds of *Camelina sativa*, *Eruca*, *Erysimum orientale*, *Sinapis arvensis*, and *S. dissecta* do not give off volatile thiocarbimide. The Indian seeds of *Brassica dichotoma*, *B. glauca*, *B. juncea*, *B. ramosa*, and the seeds of *B. napus*, *B. Rapa*, and *B. campestris* all yielded volatile thiocarbimide, but in the case of the first two and last three the odour is only slight, and does not last long.

Several different cakes were examined, the amount of thiocarbimide, the nitrogen as thiosinamine, and the melting point of the thiosinamine being determined when crystalline. It was found that all cakes which contained much rape, or seeds which do not yield volatile thiocarbimide, gave low percentages of thiocarbimide, whilst in the case of *B. Rapa* and Indian seeds the yield was decidedly higher. The determination of the thiocarbimide alone is, however, not sufficient to decide the suitability or unsuitability of a sample of cake for cattle feeding. When, however, two cakes contain the same amount of nitrogen as thiosinamine, the one which gives the larger proportion of thiocarbimide is almost sure to be the more injurious as cattle food.

As regards the percentage of nitrogen as thiosinamine, the amount required for the allyl compound (24.14 per cent.) was never reached.

Four samples, of which three were injurious, gave results very near to 22.6 per cent., whilst the nitrogen of the others was always below 22 per cent.

The melting points of these thiosinamines which crystallised showed no relation to the composition; in cases where the percentage of nitrogen was about 22.6, the thiosinamines never crystallised.

N. H. J. M.

**Decomposition of Feldspar Rocks by Roots.** By FAUSTO SESTINI (*Ann. Agron.*, 1899, 25, 399—400; from *Bull. Soc. Chim.*, [iii], 21, 515).—Gramineous plants were grown in a pot containing feldspar sand, whilst a second pot of the same sand was left without vegetation. At the end of the experiment, it was found that the pot with vegetation contained 33.5 grams of fine soil (containing 4.02 per cent. of clay), whilst the second pot contained only 14.99 grams of fine soil (containing 1.05 per cent. of clay). It is probable that microbes and algæ exercise a similar effect. It is evident therefore that biological as well as physical action is of importance in the production of soil from rocks (compare Müntz, *Abstr.*, 1887, 1135, and 1890, 1183).

N. H. J. M.

**Forms of Phosphoric Acid in Peaty Soil.** By G. NANNES (*Chem. Centr.*, 1899, i, 856—857; from *J. Landw.*, 47, 45—48).—The soil examined was well decomposed peat soil from Kalmar (Sweden), and contained: organic matter, 82.3; N, 2.66; CaO, 1.36, and  $P_2O_5$ , 0.38 per cent. Lecithin and chlorophyllan were only present in traces. Extraction with 2 per cent. hydrochloric acid yielded 0.05 per cent. of free phosphoric acid, but no phosphoric acid in organic compounds. Subsequent extraction with 10 per cent. ammonia dissolved 0.13 per cent.  $P_2O_5$ , of which 0.098 was precipitated with humus on adding hydrochloric acid. Direct extraction with ammonia (without previous acid extraction) gave 0.05 per cent.  $P_2O_5$  as free acid, and 0.133 per cent. in humus. All the percentage results refer to the original soil.

Treatment with nitric acid and precipitation of the filtrate with lead acetate yielded a substance rich in phosphoric acid. N. H. J. M.

**Solubility of the Phosphoric Acid of Surface Soil and Subsoil.** By JOSEF SEISSL (*Chem. Centr.*, 1899, i, 1136; from *Zeit. landw. Versuchswesen. Österr.*, 1899, 2, 120—134).—Phosphoric acid, total and soluble in citric acid (Maercker's method), lime, and sesquioxides were determined in a number of soil samples. In most cases, the surface soil was poorer in lime and sesquioxides than the subsoil, and it is concluded that the relation between phosphoric acid and sesquioxides is closer in the former than in the latter. The solubility of phosphoric acid is mainly influenced by the sesquioxides and organic matter, and also to some extent by the amount of lime.

Similar results were obtained with the coarser particles of soil (2—3 mm. sieve), but the amount of total phosphoric acid was so small that it is proposed, in soil analysis, to use only the fine soil (1 mm. sieve). N. H. J. M.

**The Franzenbad Mineral Peat Soil.** By ERNST LUDWIG, CARL HÖDLMOSE, and THEODOR PANZER (*Chem. Centr.*, 1899, i, 1221—1223; from *Wien, klin. Woch.*, 12, 463—468).—The humus dissolved from

the soil by alkali and precipitated by acid contained C, 58·38; H, 3·78; N, 2·1, and ash, 1·75 per cent. When distilled with steam, the soil yielded small amounts of formic and higher fatty acids. The aqueous extract of the weathered soil was strongly acid, and contained free sulphuric acid, whilst that of unexposed soil was neutral or slightly acid. The soil contains considerable amounts of pentosans.

The soil which has been long exposed to air is employed for baths, and contains much iron sulphate; in soil which has not been exposed, the iron is present as sulphide. Experiments made by Landsteiner indicate that the reduction of sulphates in peat soil is due to microbes.

Analyses of a number of samples of the soil are given.

N. H. J. M.

**Soil of Bad-Pyrmont.** By ULRICH KREUSLER (*Zeit. anal. Chem.*, 1899, 28, 411—429).—The soil contains more or less partly decomposed vegetable matter derived from marsh-plants, as well as the remains of roots and branches of woody plants. The absence of the specific peat-moss indicates the character of “meadow-moor” as opposed to peat-producing moorland. The soil is similar to that of Franzenbad and Marienbad.

The dry soil (1) not weathered, and (2) weathered, was found to contain the following percentage amounts of organic matter, &c.

	Soluble in water.			Not dissolved by water.					N.
	Ammonia.	Formic acid.	Humic acids.	Ammonia.	Humic acids.	Humin.	Wax.	Resin.	
1.	0·0095	0·0584	0·9085	0·0228	16·8195	13·2983	1·3080	0·3480	2·238
2.	0·0464	trace	1·7575	0·0183	17·0875	7·8700	1·0260	0·6610	1·562

The dry soil contained (1) 14·5144, and (2) 20·2850 per cent. of mineral matter soluble in hot hydrochloric acid of sp. gr. 1·15, and 22·8847 and 29·5624 per cent. of insoluble mineral matter. Complete analyses of the soluble (in water and in acid) and insoluble mineral matter are given for both soils. The chief differences in the amounts of substances soluble in water in the two samples are:—Ferric sulphate (1, trace; 2, 1·647), ferrous sulphate (1, 1·083; 2, 1·885), aluminium sulphate (1, 0·083; 2, 1·165), and free sulphuric acid (as SO<sub>3</sub>, 1, 0·214; 2, 0·992).

N. H. J. M.

**Occurrence of Perchlorate in Chili Saltpetre.** Injurious Action on Cereals and Sugar Beet. By AL. J. ZAHARIA (*Bied. Centr.*, 1899, 28, 511—516; from *Bul. Soc. Sci. Bucarest*, 1898, 361. Compare this vol., ii, 513).—The examination of 206 samples of Chili saltpetre at Halle showed that one sample contained 5—6, one 3—4, three 2—3, eleven 1·5—2 per cent. of perchlorate; whilst thirty-nine samples contained 1—1·5, and the rest (151) less than 1 per cent. of perchlorate.

Solutions containing 0·05—0·1 per cent. of perchlorate were found to have no effect on the germination of sugar beet, rye, and wheat, and practically no effect on barley, but a slight effect was observed in the case of oats. Even 1 per cent. solutions had very little effect on the germination of wheat.

As regards the influence of perchlorate on the development of seedlings, oats were most affected, then rye, wheat, and, least of all,



barley. A 0·001 per cent. solution had no effect on barley and wheat, but had a distinct effect on oats and rye.

The results of experiments with oats in different soils show that with Chili saltpetre containing 1 per cent. of perchlorate, the decrease of grain and straw amounted to 4 per cent. With 2 per cent. of perchlorate, the decrease in grain may be as much as 25 per cent., whilst the effect on straw production is less marked.

Sugar beet is much less affected by perchlorate than oats, and the effect may be only temporary. Even nitrate containing 6 per cent. of perchlorate will not destroy a crop of sugar beet, although it will diminish the yield of roots; nitrate containing 2 per cent. of perchlorate is not injurious, and when only 1 per cent. is present the perchlorate is even beneficial, giving an increased percentage of sugar and a somewhat higher purity coefficient. N. H. J. M.

**Denitrification and Farmyard Manure.** By ROBERT WARINGTON (*J. Roy. Agr. Soc. Eng.*, 1897, [iii], 8, 577—607).—After discussing the results of the various investigations on the subject of denitrification, and the recent results of the pot experiments of Wagner and Maercker indicating that the destruction of nitrates in the soil is the chief cause of unsatisfactory results obtained after application of dung, some results of Rothamsted experiments bearing on the question are described.

In experiments with mangel-wurzel during the six years 1878—1883, it is shown that when sodium nitrate, or ammonium salts, were applied in conjunction with superphosphate, the increase in the quantity of nitrogen in the roots, due to the nitrogenous manures, was practically the same as when they were applied in conjunction with farmyard manure (14 tons per acre per annum). The farmyard manure had therefore no depressing effect on the action of the nitrate or ammonia. This conclusion still holds good if the nitrogen of the leaves, which are returned to the land, is taken into account, since the production of the leaf is greatest on the dung plot. In more recent years, since the nitrate has been applied as a top-dressing in July, instead of being applied before the dung, the effect of nitrate in presence of farmyard manure was still greater.

Sodium nitrate and ammonium salts have a greater effect on the yield of roots without than with farmyard manure, but the increase is much less nitrogenous.

With regard to the effect of straw, further Rothamsted experiments with wheat and on permanent meadow are described, in which considerable amounts of wheat straw were applied with ammonium salts. The results do not bear out the conclusion that straw is injurious in promoting denitrification.

When very large amounts of dung are employed, as in horticulture, the danger of considerable loss of nitrogen will increase with the quantity of fermentable organic matter, and will be much aggravated by a wet condition of the land. N. H. J. M.

**Losses of the Nitrogen [of Farmyard Manure] in the Free State.** By PIERRE P. DEHÉRAIN and DUPONT (*Ann. Agron.*, 1898, 25, 401—420).—Aërobic and anaërobic fermentation experiments with

farmyard manure are described, in which weighed quantities of the manure (about 1 lb.) were kept in flasks through which air or carbonic anhydride was passed. The differences in the amounts of nitrogen in different forms before and after the experiment were ascertained, and in some cases the amounts of methane and hydrogen produced were determined.

It is concluded that whilst, as in Schloesing's experiments (Abstr., 1892, 1123), farmyard manure may ferment for several weeks without liberation of free nitrogen, other conditions may prevail under which nitrogen is eliminated. Slow fermentation, in which hydrogen as well as methane is produced, seems to be favourable to loss of nitrogen; when the fermentation is vigorous, carbonic anhydride and methane, without hydrogen or free nitrogen, are given off. To induce this vigorous fermentation, the manure must be rendered very alkaline by addition of liquid manure, and must, besides, be frequently watered. This prevents loss of ammonia, as well as of nitrogen, in the free state. Further experiments with the object of confirming this important conclusion are in progress.

N. H. J. M.

**Production of Citrate-soluble Phosphate.** By H. KNOOP (*Bied. Centr.*, 1899, 28, 516—517; from *Zeit. angew. Chem.*, 1899, 66).—The process consists in heating phosphorite, bones, &c., mixed with silicates of the alkalis (in the form of broken glass, &c.) and alkaline earths at a yellow-white heat. In the case of phosphorites containing a high percentage of phosphorus, the amounts employed are alkaline earth silicates (60) and alkali silicates (30 parts) to 100 of phosphorite. When potassium silicate is employed, the amount should be somewhat increased, and when much magnesia is present less silicate should be employed. With glass as the silicate, an addition of calcium carbonate is desirable to obtain the suitable relation of silicic acid and bases.

The fusion may be conducted in Siemens furnaces, and there is no danger of loss of phosphoric acid at high temperatures. Two mixtures of phosphorite, with chalk, sand, and sulphate, yielded products having a citrate solubility of 99 per cent.

N. H. J. M.

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## Analytical Chemistry.

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**Asbestos Filters.** By OTTO LOHSE (*Ber.*, 1899, 32, 2142—2146).—The author describes a modified asbestos filter tube constructed on the same principle as a Gooch filter (*Chem. News*, 1878, 37, 181). It consists of a glass tube, 12 cm. long and 15 mm. in diameter, closed at one end and slightly widened at the open end; the closed end is perforated with a number of minute holes, so arranged that the tube can be heated without risk of breaking. The advantage the tube appears to have over the ordinary Gooch filter is that the precipitate can be somewhat more conveniently heated in a reducing atmosphere.

Convenient forms of aluminium holder, desiccator, and tongs for removing the asbestos from the tube, are also described. J. J. S.

**Weighing Corrosive or Fuming Liquids.** By RUDOLF SCHWARTZ (*Chem. Zeit.*, 1899, 23, 451).—The apparatus is essentially a pipette, ending in two capillary tubes, and weighing about 2—3 grams. One end is placed in the liquid, and suction is applied at the other end with a pump until the bulb is three parts filled; the top tube is then sealed. By removing the pipette and turning it upside down, it becomes possible to seal the other end, and the pipette is then reweighed. The pipette may be readily broken under water to obtain the required solution.

L. DE K.

**Apparatus for the Extraction of Liquids with Ether.** By FRITZ BAUM (*Chem. Zeit.*, 1899, 23, 249—250).—Ether is boiled in a flask, and the vapour being condensed, the ether (or similar non-miscible solvent) flows down the condenser tube to the bottom of a cylindrical vessel containing the liquid (or solid matter) to be extracted. While ascending through the liquid, it dissolves any fatty matter, and when a certain quantity has collected on the top it is syphoned back into the boiling flask. An illustration is given.

When the liquid has been thoroughly extracted, it is removed with a pipette, thus leaving plenty of room for the collection of the recovered ether.

L. DE K.

**Estimation of some Inorganic and Organic Acids by means of the Volume of Hydrogen evolved on Treatment with a Metal.** By KARL ULSCH (*Chem. Zeit.*, 1899, 23, 624—625).—Platinised iron (iron powder treated with solution of platinum chloride) is quantitatively acted on by fairly concentrated solutions of sulphuric, hydrochloric, and phosphoric acids, and the amount of these acids may be readily ascertained from the volume of hydrogen evolved. Phosphoric acid causes some trouble as the platinised iron gets gradually coated with ferrous phosphate.

The process may also be extended to the estimation of oxalic, acetic, and lactic acids; the author has not, as yet, applied it successfully to tartaric and citric acid (compare this vol., i, 868).

L. DE K.

**Iodometric Acidimetry.** By FRANZ FESSEL (*Zeit. anal. Chem.*, 1899, 38, 449—453; from *Inaug. Dissert. Tech. Inst. Univ. Würzburg*, 1898).—The author has submitted to a careful study the conditions under which the reaction  $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 6\text{KCl} + 3\text{H}_2\text{O} + 6\text{I}$  can be employed for the estimation of a free acid. It is important that both the iodate and the iodide should be in excess, otherwise too little thiosulphate will be required. A deficiency of the former will be indicated by a liberation of iodine on adding iodate to the colourless liquid at the end of the titration. A deficiency of the latter is shown by the deposition of solid iodine.

Boiled water must be used, since carbonic anhydride liberates iodine from the mixture of iodide and iodate. The iodide solution (10 per cent.) should be preserved from air and light, but even if coloured by free iodine it may be used after decolorising with thiosulphate. Excessive dilution lowers the results, but as this seems to be due to a retardation of the reaction, it is recommended that where great dilution is unavoidable there should be a delay of half an hour before titrating the liberated iodine. The method cannot be employed for organic acids.

J. KJELDAHL points out that, in applying the iodometric method to the estimation of ammonia, accurate results are only obtained by working strictly in the same manner in all cases. Sulphuric acid either alone or after absorption of ammonia does not immediately liberate the theoretical amount of iodine from a mixture of iodide and iodate, but the deficiency in the quantity of thiosulphate required will be the same in the two cases if the volumes of the solutions are equal. The thiosulphate should be standardised by titrating with it the acid to be employed both before and after the absorption of ammonia from a known weight of an ammonium salt. M. J. S.

**Delicate Reaction of Hydrogen Peroxide.** By EDGAR S. BARRALET (*Chem. News*, 1899, 79, 136).—Ferrous ferrocyanide, prepared from a solution of a ferrous salt and potassium ferrocyanide, is quickly turned deep blue by hydrogen peroxide, even when the amount of the latter is as little as 1 part in 165,000 parts of water.

D. A. L.

**Estimation of Hydrochloric Acid in the Stomach Contents.** By GIUSEPPE SIRINGO (*Gazzetta*, 1899, 29, i, 476—479).—The author finds that the use of Günzberg's reagent—an alcoholic solution of phloroglucinol and vanillin (*Abstr.*, 1888, 617)—does not afford an infallible test for the presence of hydrochloric acid in the stomach contents, and suggests instead the employment of salts of nitrohydroxylamine which even in very dilute solutions are decomposed by hydrochloric and the other more energetic acids, nitric oxide being immediately evolved in almost theoretical quantity; the weak organic acids, as also acid phosphates, are without effect. 5 c.c. of the stomach contents are placed in a graduated tube which is filled with mercury and inverted in a mercury trough; a small piece of the nitrohydroxylamine salt, for instance, the sodium salt, is then introduced into the tube and after a few minutes the volume of the evolved gas is read off and corrected in the usual way. T. H. P.

**Estimation of Chlorine, Bromine, and Iodine.** By J. BOUGAULT (*J. Pharm.*, 1899, [vi], 10, 18—20).—Instead of converting the mixed silver haloids into silver chloride, they are reduced by pure metallic zinc and dilute sulphuric acid (1 of acid to 10 of water), and the precipitated metallic silver weighed. The reduction takes place easily and the results obtained are accurate. H. R. LE S.

**Detection of Chlorates, Bromates, and Iodates in the Presence of Each Other.** By DIOSCORIDE VITALI (*Chem. Centr.*, 1899, i, 1083—1084; from *Boll. Chim. Farm.*, 38, 201—209).—When manganous sulphate is treated with sulphuric acid and potassium bromate, a violet-red solution is obtained; this coloration is not due to permanganic acid, but to a manganic salt. Chlorates or iodates do not give this reaction. On boiling, the manganese is completely precipitated as hydrated dioxide.

Salts of hydroxylamine (but not the free base) act on iodates in the cold with liberation of iodine; bromates are only reduced on heating, and chlorates are not affected at all; salts of phenylhydrazine act similarly. Phosphorous and hypophosphorous acids do not act on

bromates or chlorates, but in contact with iodates, iodine is first liberated, and then redissolved as hydriodic acid. The author recommends the following process for the separation of the three compounds. By cautious addition of silver nitrate, the iodates and bromates are alone precipitated; the silver compounds are then decomposed with hydrogen sulphide, and after filtering from the silver sulphide, the excess of the former is expelled by gentle warming, and the filtrate neutralised with soda and concentrated. The iodine is liberated by means of sulphuric acid and potassium nitrite, and removed by shaking with chloroform; the liquid is then tested for bromine with chlorine water.

L. DE K.

[Detection and Estimation of Small Amounts of Iodine in Cuprite and Malachite.] By WILHELM AUTENRIETH (*Chem. Zeit.*, 1899, 23, 626—627).—The finely divided mineral is fused with 3—4 times its weight of pure sodium hydroxide (from metal) and a small quantity of water in a nickel crucible; the mass is then extracted with water, the filtered solution transferred to a glass cylinder and mixed with 10—20 c.c. of chloroform, a few drops of a 1 per cent. solution of pure sodium nitrite solution, and then acidified, while well cooled, with 20 per cent. sulphuric acid; after vigorous shaking, the colour of the chloroform solution is compared with that produced by the addition of a known quantity of potassium iodide solution (0.0001 gram iodine in 1 c.c.) to 20 c.c. chloroform, several c.c. of saturated sodium sulphate solution, dilute sulphuric acid, and a little sodium nitrite solution. The results are correct to within 0.1 milligram of iodine. If siliceous ores are present in the mineral, it is necessary to filter after fusing and rendering acid with sulphuric acid. The fusion must not be carried out at too high a temperature, as in such circumstances the sodium iodide volatilises.

J. J. S.

Detection of Fluorine in Wine. By GIULIO PARIS (*Chem. Zeit.*, 1899, 23, 685—686).—The ash obtained from 50 c.c. of wine is mixed with a little precipitated silicic acid, introduced into a platinum crucible, and 0.5—1 c.c. of sulphuric acid added. The crucible is then covered with an inverted lid containing cold water, the under side being also moistened with a drop of water. The mixture is now heated over a very small flame for 5 minutes, and when cold the drop of liquid adhering to the lid is put on to a slide covered with a thin layer of Canada balsam, and a few particles of sodium chloride are added. After about an hour, the slide is examined under the microscope for the very characteristic crystals of sodium silicofluoride.

L. DE K.

Estimation of Sulphur in Iron, Iron Pyrites, Slags, Coal, Coke, Asphalt, Rubber, and Gas Purification Material. By OTTO HERTING (*Chem. Zeit.*, 1899, 23, 768—769).—Mainly a review of recent improved methods for the estimation of sulphur in these materials.

The use of stannous chloride for reducing ferric sulphate before precipitating with barium chloride is suggested.

L. DE K.

**Estimation of Sulphuric Acid in the Presence of Iron.** By GEORG LUNGE (*Zeit. anorg. Chem.*, 1899, 21, 194—200).—An answer to Küster and Thiel (this vol., ii, 247).—A comparison of the results obtained in the estimation of sulphur in iron pyrites by the author's and Küster and Thiel's methods shows that there is no practical difference in the results obtained, being 49·93 per cent. and 49·86 per cent. respectively, and the time employed on each method is about equal. In the estimation of sulphur in pyrites residues, the results obtained by the different methods are as follows: Watson-Lunge, 1·96 per cent.; Meineke's, by fusion with sodium carbonate and potassium chlorate, 2·00 per cent.; Lunge's ammonia method, 1·94 per cent.; Küster and Thiel's, 1·94 per cent.; Meineke's, by reduction with zinc (this vol., ii, 518), 1·92 per cent. E. C. R.

**Valuation of Persulphates.** By G. H. MONDOLFO (*Chem. Zeit.*, 1899, 23, 699).—2 or 3 grams of the sample are dissolved in 100 c.c. of cold water, and 10 c.c. then heated at 60—80° in a stoppered bottle with half a gram of potassium iodide for 10 minutes. The liberated iodine is titrated with *N*/10 sodium thiosulphate, 1 c.c. of which represents 0·0114 gram of ammonium, or 0·0135 gram of potassium persulphate. L. DE K.

**Gas Washing Apparatus.** By OTTO FOERSTER (*Chem. Zeit.*, 1899, 23, 196—197).—The apparatus is based on the principle of the dephlegmator used in fractional distillation. The steam evolved when boiling a solution of an ammonium salt (such as a reduced nitrate) with excess of alkali, partly condenses, and when a certain quantity of liquid has accumulated, it is syphoned back into the boiling flask. By this means, the liquid cannot become over concentrated whilst the ammonia is still fully expelled. Two drawings are given. L. DE K.

**The Diphenylamine Test for Nitric Acid in Natural Waters.** By RAFFAELE CIMMINO (*Zeit. anal. Chem.*, 1899, 38, 429—431).—The sensitiveness of this test depends greatly on the mode of performing it. That recommended by Emmerich and Trillich has hitherto been the most sensitive, being capable of detecting nitric acid at a dilution of 1:100,000, but by the addition of a little hydrochloric acid the sensitiveness is increased tenfold. The reagent employed therefore is a solution of diphenylamine and sulphuric acid in 5 per cent. hydrochloric acid; three or four drops of this reagent are added to 1 c.c. of the liquid to be tested, then 2 c.c. of concentrated sulphuric acid, and the whole shaken. In presence of nitric acid, the mixture acquires a blue colour. No other constituent of natural water gives a similar reaction. M. J. S.

**Estimation of Ammonia and Nitric and Nitrous Acids in Natural Waters.** By LUDWIG W. WINKLER (*Chem. Zeit.*, 1899, 23, 454—455; 541).—Preferred ammonia may be estimated without previous distillation by removing the calcium and magnesium salts by means of sodium hydroxide and carbonate; the clarified solution may then be at once Nesslerised. If too little standard ammonia has been added to the comparison liquid, it does not do to add a little more, but a fresh solution must be prepared. To obviate this, and also to save the

removal of the calcium and magnesium salts, the author recommends the addition of a soluble tartrate (Rochelle salt) both to the water and to the comparison liquid.\*

The ordinary Nessler solution is not well adapted to this process, but a delicate solution may be prepared by dissolving 10 grams of mercuric iodide and 5 grams of potassium iodide in a little water, and then adding a solution of 20 grams of sodium hydroxide, and finally diluting to 100 c.c.

For the estimation of nitric acid, a slight modification of Lunge and Lwoff's process is recommended (Abstr., 1894, ii, 398). Nitrous acid is estimated by the amount of iodine liberated by the addition of hydrochloric acid and potassium iodide; the liquid is then titrated with standard solution of sodium thiosulphate, using starch-water as indicator. To get trustworthy results, the air should be excluded, which is best effected by operating in a sufficiently small flask with narrow neck, and displacing the air by carbonic anhydride generated by dropping into the acid liquid a sufficiency of solid potassium hydrogen carbonate.

L. DE K.

**A Source of Error in the Estimation of Nitric Nitrogen by Ulsch's Method.** By L. BRANDT (*Chem. Zeit.*, 1899, 23, 22).—Ulsch (Abstr., 1891, ii, 617) reduces nitrates to ammonia by the action of sulphuric acid and reduced iron. The author shows the necessity of always making a blank experiment to ascertain whether the reagents are free from nitrogen. In one case, it was found that the iron used in the experiment contained a considerable amount of nitrogen in some form capable of conversion into ammonia when the metal was dissolved in dilute sulphuric acid.

L. DE K.

**Gasometric Estimation of Nitric Oxide.** By GEORG VON KNORRE and KURT ARNDT (*Ber.*, 1899, 32, 2136—2141).—As the usual methods for the estimation of nitric oxide, namely, (1) absorption by solution of a ferrous salt; (2) titration with potassium permanganate; (3) conversion into nitric peroxide by the aid of oxygen, are considered unsatisfactory, the authors have elaborated another method which consists in passing the gas, together with an excess of hydrogen, through a Drehschmidt's platinum capillary tube heated to bright redness and measuring the contraction. According to the equation  $2\text{NO} (2 \text{ vols.}) + 2\text{H}_2 (2 \text{ vols.}) = \text{N}_2 (1 \text{ vol.}) + 2\text{H}_2\text{O}$ , the amount of nitric oxide is equal to  $2/3$  of the contraction. Very good results have been obtained by this method, but it is absolutely necessary that the mixed gases should pass very slowly through the capillary, as otherwise a certain amount of ammonia is formed. The method also admits of the estimation of nitrous oxide in the presence of nitric oxide. From the equation  $\text{N}_2\text{O} (1 \text{ vol.}) + \text{H}_2 (1 \text{ vol.}) = \text{N}_2 (1 \text{ vol.}) + \text{H}_2\text{O}$  and the one given above, it follows that if  $x = \text{vol. of nitric oxide}$  and  $y = \text{vol. of nitrous oxide}$ , then  $x + y = V$  (volume of mixture),  $1.5 x + y = C$  (contraction on leading through the capillary, and  $x = 2(C - V)$ .

\* NOTE BY ABTRACTOR.—Romijn (*Ber. Deut. Pharm. Ges.*, 1898, 8, 9) has already advocated the use of Rochelle salt.



If nitrogen is present in addition to nitrous and nitric oxides, then the amount of hydrogen used up must be determined, and the volumes of the three constituents can be calculated. J. J. S.

**Detection and Estimation of Free Phosphorus in Oils and Fats.** By ÉMILE LOUISE (*Compt. rend.*, 1899, 129, 394—395).—When a solution of silver nitrate is added to a solution of phosphorus in oil, the silver solution is reduced, and a black precipitate is produced as long as any free phosphorus is present. By previously mixing the oil with 20 times its volume of acetone, the production of any turbidity is prevented when the aqueous silver nitrate solution is added. A 10 per cent. and a 1 per cent. solution of silver nitrate are prepared, and these titrated by taking 5 grams of oil, containing a known quantity of phosphorus, and diluting to 100 c.c. with acetone. To 10 c.c. of this solution, the 10 per cent. silver nitrate solution is added drop by drop until the filtered liquid is no longer darkened in colour on the addition of another drop of silver nitrate. Suppose two drops of the silver nitrate solution were insufficient, but that after the addition of three drops the filtered liquid was not darkened on the addition of another drop, then evidently the correct amount of silver nitrate solution was between two and three drops. To determine the exact amount, another 10 c.c. of the solution are taken, two drops of the 10 per cent. solution added, the liquid filtered, and then the 1 per cent. solution added drop by drop until the filtered liquid is not darkened in colour by the further addition of silver nitrate. In this way, the strengths of the silver solutions in terms of phosphorus are ascertained. The determination of an unknown amount of phosphorus in an oil is carried out in exactly the same way. To obtain drops of exactly the same size, Duclaux's apparatus was used. H. R. LE S.

**Limits of Error in the Estimation of Phosphoric Acid Soluble in Citric Acid.** By MAX MAERCKER (*Landw. Versuchs-Stat.*, 1899, 52, 119—136).—A Report to the Verband der Versuchs-Stationen on the results of two series of determinations of phosphoric acid soluble in citric acid in samples of basic slag, the first comprising 468 analyses of 116 samples, the second 504 analyses of 252 examples.

In the second series of determinations, 92.1 per cent. showed a difference of, at most, 0.5 per cent. between the highest and the lowest result, or an error of  $\pm 0.25$  per cent. N. H. J. M.

**Estimation of Total Phosphoric Acid in Basic Slags.** By C. ASCHMAN (*Chem. Zeit.*, 1899, 23, 435—436).—The following solutions are required: nitrosulphuric acid, made by taking 420 grams of nitric acid of sp. gr. 1.2, 50 grams of strong sulphuric acid, and diluting with water to 10 litres. Solution of citric acid, made by dissolving 500 grams of the acid to 1 litre. Wagner's magnesia mixture, made by dissolving 110 grams of crystallised magnesium chloride and 140 grams of ammonium chloride in 700 c.c. of ammonia (of 8 per cent. strength) and 1300 c.c. of water. Molybdate solution, made by dissolving 150 grams of ammonium molybdate and 400 grams of ammonium nitrate to 1 litre, and pouring the solution into a litre of nitric acid of sp. gr. 1.19.

5 grams of the sample are put into a half-litre shaking bottle, which is then filled up to the mark with nitrosulphuric acid. After rotating for half an hour in a Wagner apparatus, the liquid is left overnight. 50 c.c. of the filtrate are then mixed with 10 c.c. of citric acid solution and neutralised with ammonia; 50 c.c. more water are added, and the whole left to cool for 20 minutes. To the liquid, which must be perfectly clear, are now added 20 c.c. of magnesia mixture; after a few hours standing with frequent stirring, the magnesium phosphate precipitate is collected as usual.

If the neutralised liquid deposits silicic acid, another portion of the acid solution must be precipitated with molybdate in the usual manner.

L. DE K.

**Basic Slag.** By ARMAND DEZSÖ HERZFELDER (*Landw. Versuchs-Stat.*, 1899, 52, 291—314. Compare Abstr., 1897, ii, 344).—The assimilable phosphoric acid in basic slag is in the form of tricalcium phosphate. The slag contains also calcium phosphates of higher basicity, iron phosphates, iron silicophosphates, calcium silicophosphates, calcium oxide and carbonate, silicon chiefly in combination with calcium, iron oxide, sulphide, and carbonate, &c.

The difficulties in the way of determining the tricalcium phosphate by extraction with citric acid are the presence of lime, which neutralises some of the acid, and the dissolution of a portion of the silicate, most of which is precipitated with the molybdate, redissolves in ammonia, and is again precipitated by the magnesia mixture. In this way, 0.01 and 0.02 gram of  $\text{SiO}_2$  will cause an error of 0.6 and 1.27 per cent. in the phosphoric acid. This source of error and the error (in the other direction) caused by the presence of lime, can be avoided by altering the process, but the presence of iron in the slag involves another difficulty, since iron compounds diminish the solubility of tricalcium phosphate in citric acid.

It is concluded that the error of the Wagner method is as much as 2—3 per cent., and varies according to the nature of the slag. With slags which do not contain much total phosphoric acid and silica, relatively little soluble phosphoric acid, but much lime and iron, the results will be too low; whilst with slags which contain much phosphoric acid (both total and soluble) and silica, but only a little lime and iron, the results for soluble phosphoric acid may be even higher than the total phosphoric acid.

N. H. J. M.

**Estimation of Boric Anhydride in Boracite.** By RUDOLF SCHWARTZ (*Chem. Zeit.*, 1899, 497).—Gilbert's process of carefully estimating the other constituents of the mineral and thus obtaining the boric anhydride by difference is difficult of application. Hönig and Spitz's volumetric process yields very good results. In order to prepare the solution for titration, 1—2 grams of the finely powdered sample are digested for several hours with 100 c.c. of water, and 5—10 c.c. of hydrochloric acid; if a reflux apparatus is employed, half-an-hour's heating on the water-bath will be sufficient. The filtrate is carefully neutralised with  $N/5$  soda, using methyl-orange as indicator. The solution may also be prepared by attacking the mineral suspended in water with carbonic anhydride for about half-an-hour;

after remaining for a few hours in a closed flask, the liquid is filtered, evaporated to about 20 c.c., and carefully neutralised with dilute hydrochloric acid, using methyl-orange as indicator; the carbonic anhydride is then expelled by boiling for a short time. The liquid obtained in either way is then titrated with  $N/5$  soda in the presence of glycerol, using phenolphthalein as indicator (*Abstr.*, 1897, ii, 159).

L. DE K.

**Estimation of Carbon in Iron Products.** By ADOLPHE CARNOT and E. GOUTAL (*Chem. Centr.*, 1899, i, 903; from *Anal. Chim. Appl.*, 4, 73—76).—Blair separates carbon from iron by treating the sample with a solution of potassium cuprous chloride containing 15 c.c. of hydrochloric acid in 200 c.c. The authors having tested the method, state that the temperature should not exceed  $70^{\circ}$ , otherwise there will be a loss of carbon. They, however, prefer their own process of treating the sample at  $95^{\circ}$  with the slightly acidified copper solution for about half-an-hour in a current of carbonic anhydride. Ferromanganese with more than 75 per cent. of manganese should be treated in the cold. The drying of the carbonaceous residue is often a source of decided loss.

L. DE K.

**A Rapid Eggertz Process.** By JOSEF SPÜLLER (*Chem. Zeit.*, 1899, 23, 476—478).—Some practical hints as to the quickest way of applying the well-known Eggertz test for estimating carbon in iron. The details do not admit of condensation.

L. DE K.

**Two Simple Methods for estimating Carbonic Anhydride in Quick Lime, Limestone, Animal Charcoal, Marls, &c., and Soils.** By V. SCHENKE (*Chem. Zeit.*, 1899, 23, 612—614).—The first method and apparatus present no novel features.

A new process is proposed for the estimation of carbonic anhydride combined with lime and magnesia in soils. The soil is ignited, finally over the blowpipe and the ash weighed; it is then moistened with ammonium carbonate and again dried over a low rose-burner; the increase in weight represents the carbonic anhydride in combination with the lime and magnesia.

L. DE K.

**Estimation of Potash.** By E. WIGHTMAN BELL (*Chem. News*, 1899, 79, 135—136).—In the case of manures, 5 or 10 grams are boiled with about 150 c.c. of water, with or without addition of hydrochloric acid; ammonia is then added to slight alkalinity, and is followed by barium carbonate to the extent of about double the weight of the manure taken, the boiling being continued for half-an-hour. The mixture is filtered, the precipitate is washed, and the combined filtrate and washings made up to 500 c.c., of which 50 to 100 c.c. are evaporated to dryness, along with a small quantity of ammonium oxalate, gently ignited, treated with hot water, and filtered. The filtrate is evaporated with hydrochloric acid and platinic chloride, and the estimation completed in the usual way. With soils, either the solution in hydrochloric acid is boiled, treated with ammonia, &c., as above, or the soil is moistened with strong sulphuric acid, gently ignited, boiled with water, treated with barium carbonate, boiled again, filtered, and an aliquot portion of the filtrate evaporated with

hydrochloric acid and platinic chloride, &c. The sulphuric acid treatment serves also for the estimation of potash in vegetable substances.

D. A. L.

**Estimation of Alkalis in Natural Waters.** By E. BOHLIG (*Zeit. anal. Chem.*, 1899, 38, 431—432).—Half a litre of the water is rapidly boiled down to 50 c.c. in a large porcelain basin, then strongly acidified with sulphuric acid, and evaporated without ebullition until fumes of sulphuric acid are given off. The residue is then washed into a 200 c.c. flask with 150 c.c. of water, some barium carbonate added, and carbonic anhydride passed through the mixture as long as any is absorbed; the insoluble matter is removed by filtration and washing, the filtrate evaporated to dryness, and the dry residue digested with 50 c.c. of a mixture of equal parts of alcohol and water. The alkali carbonates dissolve in this menstruum, whilst all other carbonates remain undissolved. After filtration, the total alkalis present can at once be estimated by titration with *N*/10 hydrochloric acid. The potassium is then precipitated as platinochloride, and the sodium calculated from the difference.

M. J. S.

**Estimation of the Alkalis in Urine.** By RICHARD PRIBRAM and GEORG GREGOR (*Zeit. anal. Chem.*, 1899, 38, 401—411).—With the object of establishing a method which, without loss of accuracy, should be sufficiently rapid and convenient for clinical purposes, the authors have examined the methods of Neubauer, Lehmann, Bunge, Salkowski-Munk and Heintz. Neubauer's method is far from satisfactory, Lehmann's process (*Abstr.*, 1885, 609) is theoretically free from sources of error, and as it gives higher values for the potassium found than any of the other processes, it is presumed to be the most accurate. It may be improved by substituting concentrated sulphuric acid for the ammonium sulphate added before incineration of the urine residue; a white ash is then much more rapidly obtained, and there is less danger of loss of alkali. Another improvement introduced by Kretzschmar consists in evaporating to dryness, and drying at 110° after the addition of barium chloride, ammonia, and ammonium carbonate. On treating the residue with hot water containing a little ammonia, the alkali chlorides can be washed out with great facility. Both this method and Bunge's are, however, tedious. That of Salkowski-Munk is equally so, and of lower accuracy, whilst Heintz's process is confined to the estimation of the potassium, and gives seriously low results. The authors therefore propose a new process which gives results identical with those of Lehmann, but is more rapid and requires less caution on the part of the operator. 50 c.c. of urine are mixed with 10 c.c. of dilute (1:10) sulphuric acid and a sufficient quantity of a 10 per cent. solution of barium permanganate (10—20 c.c.), and the mixture is boiled; after boiling for 10—15 minutes, a red coloration must still remain; this is removed by a few drops of oxalic acid. Barium chloride is then added in small excess followed by ammonia and ammonium carbonate; the precipitate is removed by filtration, and the filtrate evaporated in a platinum basin; the alkali chlorides thus

obtained are usually quite free from carbonaceous matter. Should magnesium be present, as may occur in all processes in which the alkalis are weighed as chlorides, it may be eliminated by keeping the chlorides at a dull red heat in a covered platinum crucible for an hour or longer, by which means magnesium chloride is converted into oxide. It is then desirable to estimate the total chlorine by silver, and the potassium by platinum, and calculate the sodium indirectly.

M. J. S.

**Separation of Zinc from Nickel.** By E. DÖHLER (*Chem. Zeit.*, 1899, 23, 399—400).—Zinc may be separated from nickel by precipitation with hydrogen sulphide in the presence of free acetic acid when mineral acids are absent. Good results may be obtained by using a very large excess of acetic acid, but even then the precipitated zinc sulphide may be of a dark colour and contain an admixture of nickel sulphide. It may be freed from nickel by dissolving it in dilute hydrochloric acid, which leaves most of the nickel sulphide undissolved, and after neutralising the filtrate with ammonia and adding sodium acetate and free acetic acid, again precipitating by means of hydrogensulphide, pure white zinc sulphide being then obtained. Instead of using sodium acetate and acetic acid, the neutralised solution may be advantageously mixed with sodium formate and formic acid; the precipitate produced by hydrogen sulphide is then free from nickel, and needs no purification.

L. DE K.

**Electrolytic Estimations and Separations.** By LILY G. KOLLOCK (*J. Amer. Chem. Soc.*, 1899, 21, 911—928).—Some of the older methods for electrolytic determinations and separations in potassium cyanide solutions have been repeated. The exact conditions as to current density, ampère and voltage and other factors have been worked out for the estimation of cadmium, silver, and mercury, and for the separation of silver, mercury, or gold from platinum, copper, zinc, nickel, or cobalt; of silver or mercury from cadmium or iron, and of gold from palladium.

Mercury may be deposited from alkali sulphide solution under the following conditions: 25 c.c. of sodium sulphide are added to a solution of mercuric chloride containing 0.1403 gram of mercury; this solution, diluted to 125 c.c., is electrolysed at 70° by a current of  $N.D._{100} = 0.11$  ampère, and voltage = 2.5, and, at the end of 5 hours, the mercury is completely deposited. Copper can be deposited from nitric acid solution by using a current of  $N.D._{100} = 0.09$  and voltage = 1.9 in 5 hours at 65°; mercury can also be deposited in a similar manner.

Cadmium is deposited from sulphuric acid solution in 5 hours at 65° when a current of  $N.D._{100} = 0.078$  and voltage = 2.61 is employed. Mercury may also be estimated in a somewhat similar manner.

The conditions necessary for the accurate determination of bismuth in citric acid, ammonium citrate, or potassium citrate solution have also been determined. In the case of ammonium citrate, the solution is made ammoniacal and is electrolysed at 65°, first with a current of 0.02 ampère and 1.8 volts, the current being finally increased to

0.09 ampère and 2.3 volts. A certain amount of bismuth peroxide is always deposited on the anode and must be weighed. A current of much the same density was employed in both citric acid and potassium acetate solutions, and in the latter case the solution was made strongly alkaline by the addition of potassium hydroxide.

Iron may be deposited in the course of 7 hours from a solution containing sodium citrate and free citric acid when a current of 0.58 ampère and 5.7 volts is employed, or in 4.5 hours at 50° with a current of 0.4—1 ampère and 7—11 volts. J. J. S.

**Precipitation of Cadmium by Hydrogen Sulphide.** By ROBERT MELDRUM (*Chem. News*, 1899, 79, 170—171).—The author attributes failure to detect small quantities of cadmium, by means of hydrogen sulphide in the way usually employed, to the too liberal use of hydrochloric acid, which dissolves the sulphide. He has further investigated the precipitation by means of hydrogen sulphide of neutral solutions of cadmium sulphate varying in strength from 0.5 to 0.00125 per cent. Solutions from 0.5 to 0.25, in the cold give a curdy precipitate which settles quickly and a dense, opaque, yellow solution; when heated to boiling, the precipitate becomes orange-yellow, settles rapidly, and turns paler on cooling, but does not regain its former colour; the solution is clear with a slight yellow tinge. Agitation while cooling, and when cold, makes the precipitate settle less rapidly and renders the solution opaque. Solutions containing from 0.2 to 0.02, yield less precipitate on boiling, give little or no precipitate in an hour in the cold, and the solution remains opalescent. Solutions of greater dilution (except the 0.00125, which shows no colour in a thickness of 2 inches) yield yellow solutions, but no immediate precipitate. The filtrates from the solutions of greater strength than 0.0175 per cent. are almost free from colour in a thickness of 2 inches, but from the solutions of still greater dilution the filtrates are always coloured. By repeated filtrations, this colour may be removed from the 0.0175 to the 0.015 per cent. solutions but not from the weaker filtrates; these, however, deposit a small precipitate in 24 hours, but still retain a yellow colour.

A colorimetric method of estimating cadmium is suggested for solutions not exceeding in strength 0.02 per cent. of the sulphate.

D. A. L.

**Solubility of Lead Sulphate in Aqueous Ammonium Acetate.** By J. C. LONG (*Amer. Chem. J.*, 1899, 22, 217—218).—Lead sulphate is most soluble in a solution of ammonium acetate containing 33 grams per 100 c.c. To dissolve lead sulphate in analysis, it is best to add, for each gram, 10 c.c. of the ammonium acetate solution, heat to boiling, and filter promptly; to recover the lead sulphate, 0.5 gram of sulphuric acid should be added, this facilitating the evaporation and expulsion of the ammonium acetate. W. A. D.

**Separation of Copper and Zinc.** By W. DEDERICHS (*Chem. Centr.*, 1899, i, 950; from *Pharm. Zeit.*, 44, 198).—Zinc is estimated in brass by dissolving in the smallest possible amount of nitric acid,

diluting with water containing 2—3 per cent. of hydrochloric acid, and removing the copper by means of hydrogen sulphide; the filtrate is then boiled and the zinc precipitated with sodium carbonate.

To estimate copper, the nitric acid solution of the brass is digested with sodium hydrogen sulphite, and an excess of a standard solution of ammonium thiocyanate is added to precipitate the copper; the excess of the reagent is then titrated with silver nitrate in an aliquot part of the filtrate.

Traces of lead are estimated in the usual way as sulphate.

L. DE K.

**Separation of Copper from Cadmium as Oxalate.** By G. BORNEMANN (*Chem. Zeit.*, 1899, 23, 565—566).—The solution of copper and cadmium, which must not be too concentrated, is mixed with a moderate quantity of nitric acid, heated to boiling, and then mixed with a slight excess of oxalic acid previously dissolved in boiling water; the liquid is then placed in a water-bath until it has become quite clear. The precipitated copper oxalate is first washed by decantation with boiling water containing a little nitric and oxalic acids, and then collected on a suitable filter and washed with boiling water containing at first a few drops of oxalic acid; in this way, the precipitate is obtained free from cadmium. The oxalate is finally converted into sulphide by ignition with sulphur in a current of hydrogen.

L. DE K.

**Modification of Eschka's Mercury Assay.** By K. E. CHISM (*Chem. Centr.*, 1899, i, 996; from *Trans. Amer. Inst. Min. Eng.*, Oct., 1898).—Eschka's method of mercury assay by collecting the mercury vapour on a weighed golden lid, gives accurate results, but is somewhat expensive, as the gold soon wears out. The author now substitutes a lid made of silver of about 0.02 mm. thickness; this may be used three times, and costs but little.

0.5—1 gram of the ore is mixed in a porcelain crucible with 5 grams of clean iron filings, another gram of the iron being sprinkled on the top. The crucible is placed on a perforated plate and the lid is put on, and cooled by placing on it a silver or copper basin filled with cold water. The bottom of the crucible is now heated for 15 minutes with a spirit lamp, and when cold the lid is taken off and re-weighed. On applying heat, the mercury volatilises, and the lid may be used again.

L. DE K.

**Volumetric Estimation of Manganese in Manganates by means of an Alkaline Solution of Arsenious Acid.** By C. REICHARD (*Chem. Zeit.*, 1899, 23, 801—802).—The process is based on the fact that on adding an alkaline solution of arsenious acid of known strength to a solution of a manganate, the latter is reduced to manganous hydroxide. The unoxidised arsenious acid is then estimated by standard iodine; or the manganous hydroxide may be at once redissolved by adding sulphuric acid and the arsenious acid then estimated in acid solution with standard permanganate.

Five molecules of arsenious acid used for reduction are equivalent

to four atoms of metallic manganese. The test experiments are satisfactory. L. DE K.

**The Presence of Carbon in Electrolytically Deposited Iron.** By SAMUEL AVERY and BENTON DALES (*Ber.*, 1899, 32, 2233—2238. Compare this vol., ii, 251, and Verwer and Groll, *ibid.*, 387)—The authors maintain the accuracy of their former conclusion that the ordinary methods for the electrolytic estimation of iron do not yield satisfactory results, because a small amount of iron remains in the solution, and the deposited metal contains carbon.

In the presence of oxalic acid, the reaction with potassium thiocyanate is not delicate, and cannot therefore be depended on for indicating the completion of the deposition. Oxalic acid is converted by electrolytic reduction into glycollic acid, and the presence of this in the solution causes the deposited metal to contain carbon. A. H.

**Potassium Ferrocyanide as a Source of Iron in the Volumetric Analysis of Iron.** By K. SCHRÖDER (*Chem. Zeit.*, 1899, 23, 533—534, 540—541, 557—559).—The author states that potassium ferrocyanide may be obtained almost absolutely pure and be advantageously utilised as a source of pure iron when standardising solutions for the technical estimation of iron.

Four or five grams of the pure salt are heated in a Kjeldahl flask with 20—25 c.c. of strong sulphuric acid; heat is applied, moderately at first, and then gradually increased until boiling sets in, which is then kept up for half-an-hour. When cold, 25 c.c. of water and 10—15 c.c. of hydrochloric acid of sp. gr. 1.19 are added and the mixture warmed until completely dissolved. This solution may now be reduced with zinc, or by means of stannous chloride followed by mercuric chloride, and will then be fit for standardising purposes. L. DE K.

**Estimation of Iron in Organic Matter.** By FRANZ RÖHMANN and FRANZ STEINITZ (*Zeit. anal. Chem.*, 1899, 38, 433—435).—Instead of destroying the organic matter by incineration, it is far preferable to employ Neumann's method of heating with concentrated sulphuric acid and ammonium nitrate. The operation is performed in a Jena glass flask over the naked flame, the ammonium nitrate (1 gram for each c.c. of acid) being added in several portions, and the heating continued until a clear, pale yellow liquid is obtained. This is now made alkaline with ammonia and the iron precipitated as sulphide by adding a few drops of colourless ammonium sulphide with the usual precautions. The iron sulphide is collected on an ash-free filter, from which it is redissolved by sulphuric acid, the solution being run back into the precipitation flask, where it dissolves any iron sulphide adhering to the sides. Here it is concentrated by boiling and transferred to a platinum basin, in which, meanwhile, the filter has been incinerated and its ash fused with potassium hydrogen sulphate. By introducing a rod of zinc for about half-an-hour, the ferric salt is completely reduced, and is then titrated with permanganate.

In dealing with faeces, the large amount of calcium sulphate formed is an inconvenience. It is best not to attempt to remove it from the



original acid solution, but to precipitate the iron sulphide in the turbid liquid. Urine (300—400 c.c.) should be mixed with 25—30 c.c. of fuming nitric acid and boiled down to a small volume before adding sulphuric acid (20—30 c.c.) and ammonium nitrate. M. J. S.

**Iron Separations with Alkali Salts. I.** By HARRY BREARLEY (*Chem. News*, 1899, 79, 193—194).—It is pointed out that for the separation of iron from manganese, zinc, nickel, cobalt, and sometimes copper, alkali acetates, phosphates, sulphates, chromates, tungstates, and molybdates are amongst the available reagents. *Separation with acetates* has already been investigated (Abstr., 1896, ii, 676; 1897, ii, 388; 1898, ii, 96 and 143); it is, however, now shown that it is best not to add the acetate to the cold solution, and then to heat to boiling, but that the acetate should be added to the hot solution. Furthermore, it is shown that with a constant quantity of nickel or other metal and varying quantities of iron, the exactness does not necessarily increase with the decrease in the proportion of iron; but with fixed proportion of iron and a varying proportion of nickel, probably the separation is better for small than for large amounts of nickel.

D. A. L.

**Detection of Cobalt in the Presence of Ferric Compounds.** By HENDRIK WEFERS BETINK (*Chem. Centr.*, 1899, i, 904; from *Ned. Tydschr. Pharm.*, 11, 64—66).—When a solution of cobalt is mixed with potassium thiocyanate and a mixture of ether and alcohol poured on to the surface, a blue coloration is observed in the upper layer. In the presence of ferric salts, however, the red colour given by ferric thiocyanate interferes with the test, but in this case the iron compound may be removed by first extracting the mixture with pure ether, which dissolves the ferric thiocyanate but not the cobalt compound; the ether-alcohol mixture is then added to the residual liquid.

The author has improved the method by operating as follows: Potassium thiocyanate is added and the red coloration is destroyed by adding powdered sodium thiosulphate; the liquid is then covered with a layer of ether-alcohol. 0.001 gram of cobalt nitrate may thus be detected in the presence of 1 gram of ferric chloride.

L. DE K.

**Reduction of Chromic Acid by Acetic Acid and its Effect in Anthracene Testing.** By HENRY BASSETT (*Chem. News*, 1899, 79, 157).—When the mixture of acetic acid with chromic acid used in anthracene testing is stored, the latter suffers some reduction, a reaction that is still more marked when undiluted acetic acid is boiled with chromic acid; but it also takes place with aqueous solutions of acetic acid when boiled, not, however, when the volumes of the acetic acid and water are equal. The reduction is more marked with acid crystallising at 13.5° than with the purer acid crystallising at 17°.

In anthracene testing, the less pure acetic acid and mixed solutions of acetic and chromic acids that have been kept too long (more than 15 days) will give results which are too high.

D. A. L.

**Testing Oil of Turpentine for Mineral Oils.** By C. SCHREIBER and F. ZETZSCHE (*Chem. Zeit.*, 1899, 23, 686—687).—The following

method is suggested as a good preliminary test: 1 c.c. of the sample of turpentine is diluted to 50 c.c. with alcohol of 90—95 per cent. 20 c.c. of this solution are put into a 75 c.c. glass cylinder and 20 c.c. of a solution containing exactly 15 grams of potassium bromate and 50 grams of potassium bromide in a litre are added, followed by 20 c.c. of dilute sulphuric acid (1:3). The stopper is inserted and the mixture well shaken for half a minute. If the liquid should not be quite decolorised, the sample is likely to contain mineral oil and should be submitted to further analysis, but otherwise it may pass as commercially pure.

L. DE K.

**Estimation of Dry Substance in Glycerol.** By G. BENZ (*Zeit. anal. Chem.*, 1899, 38, 436—438).—It is commonly accepted that glycerol cannot be estimated by drying at 100°, because the glycerol begins to volatilise as soon as all the water has evaporated. The author shows, however, that this occurs only in shallow, uncovered vessels. By employing a wide-necked flask covered with a loose glass cap resting on the neck, glycerol can be dried to a constant weight either at 100° or 110°, and that this takes place without loss is shown by dissolving glycerol, so dried, in water and re-evaporating the solution in the same flask, when exactly the same weight of dry substance will be obtained.

M. J. S.

**Estimation of Glycerol in Fermented Liquids.** By J. B. VINCENT LABORDE (*Chem. Centr.*, 1899, i, 905—906, 1086; from *Ann. chim. anal. appl.*, 4, 76—80; 110—114. Compare *Abstr.*, 1896, ii, 77).—The process is based on the fact, noticed by the author, that at 150—200°, glycerol is quantitatively decomposed by sulphuric acid with liberation of the whole of the carbon; 1 part of carbon represents 2.56 parts of glycerol. A quantity of liquid containing from 0.1—1.0 gram of glycerol is mixed with 10 drops of sulphuric acid and boiled down in a 250 c.c. flask with small, flat bottom until about 2 c.c. are left. 6 c.c. of sulphuric acid are then added and the flask closed with a rubber cork through which passes a glass tube drawn out to a fine point. The mixture is now heated on a sand-bath to 150°, and when the action takes place the temperature rises to 200°. After a few minutes, 5 c.c. of dilute hydrochloric acid (1:1) are added, and the whole is heated on the sand-bath until white fumes begin to form; the carbon is now thoroughly washed by decantation with boiling water, and then transferred to a weighed platinum dish; a little ammonia is added, and the whole dried first at 110° and then over a small rose-burner until no more ammoniacal odour is noticed. When cold, the carbon is weighed and allowance made for any ash.

To estimate glycerol in saccharine liquids, any sugar must first be removed. If the amount does not exceed 0.5 gram per litre, 50 c.c. are mixed with 100 grams of small shot, evaporated down to 2—3 c.c. and gradually mixed with 1—2 grams of calcium hydroxide; 75 c.c. of ether-alcohol mixture (2:1) are then added to dissolve the glycerol; the liquid is filtered, and the residue is washed with more of the ether mixture until the filtrate reaches 200 c.c. After adding 10 drops of sulphuric acid, the ether-alcohol is distilled off and the residue treated as already described.

If the amount of sugar amounts to 5—20 grams per litre, the sufficiently concentrated solution is mixed with 2 grams of calcium hydroxide which has been moistened with alcohol; if the mass does not readily set, a little more dry lime should be added; the mass must then be extracted as before with ether-alcohol mixture. If the liquid contains more than 20 grams of sugar per litre, a volume of it which will contain about 5—6 grams of sugar is mixed with 2 grams of calcium hydroxide suspended in 10—20 c.c. of proof spirit and then boiled with 100—200 c.c. of 80 per cent. alcohol. When cold, an aliquot portion of the filtrate is acidified with tartaric acid, and the alcohol having been expelled, the residue is treated as before with the ether-alcohol mixture.

The test analyses are very satisfactory.

L. DE K.

**Behaviour of Iron Salts with Pyrogallol.** By A. HIRSCH (*Chem. Centr.*, 1899, i, 927; from *Pharm. Zeit.*, 44, 205).—When 2 drops of a solution of ferric chloride containing 10 grams of liq. ferri. sesquichlor., in 90 of water are added to a few c.c. of a 1 per cent. solution of pyrogallol, an amethyst-blue coloration is first formed, which rapidly changes to reddish-brown, but if 1 c.c. of a 0.1 per cent. solution of sodium hydroxide or 0.5 c.c. of a 0.5 per cent. solution of sodium carbonate be then added, the solution becomes deep blue. The brown coloration is restored, however, by adding very small quantities of mineral acids. Zinc oxide or barium carbonate acts like the alkalis, hence the brown coloration must be due to the mineral acid contained in the ferric salt. Organic iron salts give blue colorations, which become brown only on addition of mineral acids. A solution of pyrogallol, rendered reddish-brown by the addition of a very dilute solution of ferric chloride, may be used to test for faint alkalinity, as, for instance, in the case of dilute solutions of alkaloids, which give the blue coloration. When pure ferrous salts are mixed with solutions of pyrogallol, a white turbidity is formed, and if a very dilute solution of sodium hydroxide is then added, the solution becomes blue, probably owing to partial oxidation of the ferrous salt.

E. W. W.

**Estimation of Mannose in Mixtures of Sugars.** By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1899, 129, 339—341).—The solution of mannose is mixed with a solution of equal volumes of phenylhydrazine and glacial acetic acid, allowed to remain for 8 hours at the ordinary temperature, and the precipitate washed successively with ice-cold water, alcohol, and ether, and dried in a vacuum. The results are not affected by the presence of galactose, arabinose, maltose, or dextrin, and are accurate if the solution contains 3 to 6 per cent. of mannose, and the operations are conducted at as low a temperature as possible. A correction should be made by adding 40 milligrams to the weight of the precipitated hydrazone for every 100 c.c. of solution.

C. H. B.

**Influence of Sucrose on the Estimation of Pentosans by the Phloroglucinol Method, with special reference to Products from Sugar Refineries.** By KARL ANDRLIK (*Chem. Centr.*, 1899, i, 905; from *Zeit. Zuck. Ind. Böhm.*, 23, 314—323).—When pentoses

are estimated by the phloroglucinol method, the result, calculated as arabinose, may be from 0.60—0.89 per cent. too high if cane sugar is present.

Substances yielding furfuraldehyde are found in the diffusion syrup to the extent of only 0.2 part for every 100 parts of cane sugar; the concentrated juice contains 0.13, and the first crop of crystals 0.03 part; the greater portion of these passes into the "scum" or the molasses.

L. DE K.

**Cobalt Derivatives of Sucrose and of Dextrose.** By W. HERZOG (*Chem. Zeit.*, 1899, 23, 627—628).—Papasogli (Abstr., 1898, 194) states that an aqueous solution of cane-sugar, when treated with a few drops of a solution of a cobalt salt and then with an excess of sodium hydroxide, gives an amethyst-violet coloration which is moderately stable, whereas an aqueous solution of dextrose, when treated in the same manner, yields a blue colour which is remarkably evanescent, changing quickly to a dirty green, and he recommends this reaction as a test for sucrose in the presence of dextrose. The author finds that the colours produced in the two cases are very similar, that with dextrose, however, is not so stable—it immediately turns blue and then a dirty green; with saccharose, too, the final colour is dirty green. The method is therefore of no use in testing for sucrose in the presence of dextrose. With regard to the nature of the products, it is thought probable that they are compounds of the cobalt salts with alkali sucrates or dextrosates, the colour depending to a certain extent on the actual cobalt salt employed.

J. J. S.

**Analyses of Honey.** By C. HOITSEMA (*Zeit. anal. Chem.*, 1899, 38, 439—441).—In 10 samples of honey of known origin, the following estimations have been made: (1) specific gravity at 15° of a filtered solution of 1 part of honey in 2 parts of water; (2) pollen and wax, the constituents insoluble in warm water; (3) moisture estimated by drying without heat in a vacuum desiccator; (4) polariscopic rotation (after König, *Unters. landw. gew. wicht. Stoffe*, 1898, 474; (5) ash; (6) reducing and invertible sugars. The sp. gr. ranged from 1.102 to 1.14, water from 8.3 to 17.8 per cent.; polarisation from -3.1 to -9.1, being in all cases negative, ash, 0.12 to 0.34 per cent., pollen and wax, 0.02 to 0.46 per cent.; reducing sugar, 71.2 to 74.4; and sucrose, 0.2 to 2.6 per cent., whilst a sample of unknown origin showed 6.4 per cent. of the latter.

M. J. S.

**Estimation of Sugar in Fodder containing Molasses.** By OTTO FOERSTER (*Chem. Zeit.*, 1899, 23, 196).—The analysis is generally made by mixing a weighed quantity of the sample with water up to a definite volume, and afterwards making a correction for the volume of the undissolved matter; but this process can hardly lay claim to accuracy. The author recommends weighing out a multiple of 13.024 grams of the fodder and then extracting this in a Sickel's apparatus with absolute alcohol; after 12 hours, it may be taken for granted that all the sugar has been extracted. After distilling off the spirit, the residue is dissolved in water and diluted to a volume representing 75 c.c. for each 13.024 grams of the sample, and the sugar is then estimated either chemically or polarimetrically.

L. DE K.

[**Estimation of Caramel.**] By N. FRADISS (*Chem. Centr.*, 1899, i, 1160—1161; from *Bull. de l'Assoc.*, 16, 280).—The amount of caramel contained in sugar products is determined by treating the dry substance with a small quantity of methylic alcohol of 95°, evaporating on the water-bath, drying the gummy residue in a vacuum or in a current of dry air, and again digesting it with methylic alcohol for 2 hours. The caramel is precipitated from the solution by amylic alcohol, the precipitate redissolved, reprecipitated once or twice more, and finally dried at 90° and weighed. The caramel may also be determined by titrating with Violette's or Fehling's solution, but if dextrose is present it is necessary to titrate the original solution before and after treating with an excess of lead acetate. Then if  $A$  = c.c. of copper solution required,  $a$  = c.c. of original solution required for 5 c.c. of copper solution, the volume of the copper solution corresponding with the caramel is  $5(1 - a/A)$ . Allowance must also be made for the amount of lead acetate solution (1/10 vol.) used. The dextrose may also be destroyed by boiling with calcium carbonate and then precipitating with carbonic anhydride. Traces of caramel are estimated by treating 200 c.c. of the solution with excess of ammoniacal lead acetate. The precipitate, after washing with water free from carbonic anhydride, is suspended in water and decomposed with hydrogen sulphide. The filtrate is again treated with lead acetate, and the solution, from which the hydrogen sulphide has been expelled by evaporating to 10 c.c., is titrated with copper solution. Determinations of the amount of caramel in various sugar products are quoted. E. W. W.

**Estimation of Glycogen.** By EDUARD PFLÜGER and JOSEPH NERKING (*Pflüger's Archiv*, 1899, 76, 531—542. By EDUARD PFLÜGER, *ibid.*, 543—551. Compare this vol., ii, 529).—These two papers contain more criticisms of Külz's method, and show that it can be improved by certain modifications. A new method, which is simpler and gives practically the same results as the improved Külz method, depends on the fact that in an alkaline solution of glycogen, or extract of flesh or liver, alcohol will completely precipitate the glycogen, and if the solution contains potassium iodide, the proteid matter remains in solution. W. D. H.

**Detection of "Saccharin" in Foods.** By ALFRED HASTERLIK (*Chem. Zeit.*, 1899, 23, 267—268).—The author, having tried a large number of sweetened beverages for "saccharin" by Börnstein's resorcinol test, finds that this process is absolutely worthless, as the green fluorescence is often obtained when the liquids are quite free from "saccharin," as proved by other tests. The green colour is often caused by succinic acid, traces of which are always present in fermented liquids. L. DE K.

**Detection of Formaldehyde in Milk.** By ALEXANDER LEYS (*J. Pharm.*, 1899, [vi], 10, 108—114).—Gayon's solution (*Abstr.*, 1888, 326), as used by the author for the detection of small quantities of formaldehyde in milk, is prepared by adding 10 c.c. of pure hydrochloric acid to a mixture of 10 c.c. of sodium hydrogen sulphite solu-

tion (30° B.) and 1000 c.c. of a 0.1 per cent. aqueous solution of magenta. It produces a well marked coloration with the distillate from milk containing one part of formaldehyde in a million.

H. R. LE S.

**Estimation of Formaldehyde by the Aid of Hydrogen Peroxide.** By OSKAR BLANK and HERMANN FINKENBEINER (*Ber.*, 1899, 32, 2141. Compare this vol., ii, 188).—A reply to Harden's criticism (*Proc.*, 1899, 15, 158). The authors' contention that their method is extremely accurate has been proved by numerous determinations.

J. J. S.

**Iodine Number of Fatty Acids.** By ALEXANDER ZEGA and R. MAJSTROVIĆ (*Chem. Zeit.*, 1899, 23, 597).—From experiments with fatty acids from maize oil, olive oil, sesamé oil, and cotton seed oil, the conclusion is drawn that the iodine number largely decreases when the fatty acids are kept too long in the air-bath. In the case of maize oil, it was found that the dried acids, when kept at the ordinary temperature for some days, gave a gradually decreasing iodine number, falling in 8 days from 118.6 to 102.3 per cent.

L. DE K.

**Modification of Kaemer's Method for the Analysis of Cream of Tartar.** By G. LOMBARD (*Chem. Centr.*, 1899, i, 1086; from *Staz. sperim. agrar. ital.*, 32, 123—126).—In Kaemer's method, a weighed quantity of the sample is dissolved in the calculated amount of normal soda, the solution diluted to 200 c.c., and 20 c.c. are acidified with acetic acid and evaporated to dryness; the residue is washed with alcohol until the washings are no longer acid, and the undissolved potassium hydrogen tartrate then estimated by means of standard alkali.

The author has successfully modified this test. 20 c.c. of the solution are mixed with 1.5 c.c. of acetic acid and then with 100 c.c. of a mixture of equal parts of commercial absolute alcohol and ether. After the lapse of 4 hours, the potassium hydrogen tartrate has separated completely, and may be freed from acid by washing with ether-alcohol mixture; it is then titrated as before.

L. DE K.

**Calcium Citrate and its Analysis.** By ARTURO SOLDAINI and E. BERTÈ (*Gazzetta*, 1899, 29, i, 489—497).—The authors assign the considerable differences found in the results of analyses by different workers of commercial calcium citrate to two causes. Firstly, the amount of water retained by the sample varies with the method of storage, with the time of exposure to the air, &c. Secondly, when estimated as calcium citrate, the solubility of the latter in the washing water is not properly allowed for. Error is also sometimes caused by excessive drying of the citrate which then becomes to a slight extent insoluble in acetic acid. The authors find that crystallised calcium citrate loses  $2\text{H}_2\text{O}$  at 100—130°, and the remaining  $2\text{H}_2\text{O}$  at 175—185°. The following method of analysis is recommended. 1 gram of the finely powdered substance is heated in an Erlenmeyer flask with 10 c.c. of water, about 20 drops of hydrochloric acid of sp. gr. 1.18 added, and when solution has taken place, the liquid is cooled, made distinctly alkaline to phenolphthalein with  $N/2$  sodium hydroxide, and then about 3 c.c. of acetic acid added. The liquid is filtered and the residue washed until it is no longer acid to litmus paper.

The filtrate is evaporated to dryness on the water-bath, the dry mass being taken up with 15–20 c.c. of boiling water and the solution filtered on a hot water funnel through an ashless filter of 9 cm. diameter. The residue is then washed with 55 c.c. of water in such a way as to have the last drops of the washings almost or quite colourless. The precipitate is dried, burnt, and calcined strongly for 10 minutes.

T. H. P.

**Estimation of Non-volatile Organic Acids in Tobacco.** By RICHARD KISSLING (*Chem. Zeit.*, 1899, 23, 2–4. Compare Abstr., 1898, ii, 659).—I. *Separation and estimation of oxalic, citric, and malic acids by the baryta method.*—The barium salts of these acids may be obtained practically anhydrous by drying them at 70° under 100 mm. pressure; they then yield almost the theoretical amount of barium carbonate. Calcium oxalate also becomes quite anhydrous when thus treated.

The mixed acids are titrated with standard baryta, and 20 per cent. by volume of alcohol is then slowly added with constant stirring. Barium citrate and oxalate are almost completely precipitated, whilst the malate practically remains in solution, the two errors fairly compensating each other. The malate is then recovered from the filtrate by adding alcohol until its amount reaches 70 per cent. by volume, and leaving the mixture for 24 hours. Both precipitates are collected and weighed. The oxalic acid is estimated in a fresh portion of the solution of the acids by precipitation with calcium chloride in the presence of ammonium acetate.

II. *Estimation of oxalic, citric, and malic acids in tobacco.*—The process (*loc. cit.*) has been slightly modified. The first extraction of the tobacco with ether is now continued for 40–50 hours, and then again for 20 hours, this being repeated two or three times. After making up to 200 c.c., it is better to use 50 c.c. in place of 25 c.c. After shaking out the ether with 90 c.c. of water, the acids are separated as already described.

L. DE K.

**Influence of the Quality of the Ether on the Estimation of Fat in Food-stuffs.** By THEODOR METHNER (*Chem. Zeit.*, 1899, 23, 37–38).—When foods contain substances readily soluble in water or alcohol, it is as well to extract the fat by means of ether which is free from either water or alcohol. Absolutely anhydrous ether may be obtained by allowing ether to stand over metallic sodium, but the author states that a very good ether may be prepared by placing the commercial article of sp. gr. 0.720 for three weeks over quicklime and then distilling. This will extract about 0.1 per cent. more than the ether prepared by means of sodium.

L. DE K.

**Estimation of Fat in Animal Organs.** By WILHELM KNÖPFEL-MACHER (*Chem. Centr.*, 1899, i, 860–861; from *Österr. Chem. Zeit.*, 2, 122–124. Compare Dormeyer, Abstr., 1895, ii, 540; Frank, 1898, ii, 174; Voit, *ibid.*, 175).—Fat occurs in organs in two forms, one readily extractable with ether, whilst the other seems to be mechanically combined with proteid matters and cannot be extracted by the Soxhlet apparatus in 1000 hours. According to the

author, the best plan is to digest the matter with pepsin; this dissolves the proteids and so renders all the fat soluble in ether.

L. DE K.

**Preservation of Hübl's Reagent.** By RANDOLPH BOLLING (*Amer. Chem. J.*, 1899, 22, 213—214).—The author's experiments show that the alteration of Hübl's reagent as regards the free iodine present is very rapid and is only slightly delayed by using absolute alcohol in preparing it or by excluding air and light. W. A. D.

**Estimation of Fat in Milk.** By RICHARD WINDISCH (*Landw. Versuchs-Stat.*, 1899, 52, 209—211).—A number of samples of milk were analysed by the methods of Liebermann and Székely (*Abstr.*, 1893, ii, 308) and Gerber. The results, which are given, indicate that both methods are satisfactory. N. H. J. M.

**Aërometric Estimation of Fat in Milk.** By H. TIMPE (*Chem. Zeit.*, 1899, 23, 436—437, 455—457. Compare *Abstr.*, 1895, ii, 95).—When milk is mixed with aqueous potash, a small but fairly definite quantity of the fat is saponified and becomes insoluble in ether; this constitutes a slight error in Soxhlet's aërometric process. Another slight source of error is the fact that the usual figures representing the mutual solubility of ether and water are not absolutely correct. Finally, the following modified formulæ are proposed:

(1)  $Z = A - 0.075 W$ ; (2)  $F = 1.4566 Z \frac{S - 0.7222}{(0.9520 - S) \frac{v}{100}}$ , where  $A$  represents the weight of the ether saturated with water,  $W$  the weight of the water,  $Z$  the weight of the aqueous ether left after shaking,  $S$  the sp. gr. of the ethereal fat solution,  $v$ , the original volume of the milk,  $s$ , its sp. gr., and  $F$ , the weight of the fat it contains.

L. DE K.

**Estimation of Fat in Milk.** By A. A. BONNEMA (*Chem. Zeit.*, 1899, 23, 541—542).—10 c.c. of milk are put into a 100 c.c. cylindrical glass and mixed with 1.5 c.c. of aqueous caustic potash (20 grams per 100 c.c.). After shaking for a moment, 25 c.c. of ether are added and the whole thoroughly shaken for 5 minutes, the glass being held in the warm hand. The glass is placed in cold water, the stopper removed for a moment, 2 grams of tragacanth are added, and the whole is again thoroughly shaken. The tragacanth absorbs all the water and forms a clot, whilst the ether becomes quite clear; 10 c.c. of the ethereal solution are now pipetted off and evaporated in a weighed dish. The results agree with those obtainable by the "Gerber process."

L. DE K.

**Varying Composition of Butter.** By J. J. L. VAN RIJN (*Chem. Zeit.*, 1899, 23, 453—454).—The results obtained by the author again confirm the fact that the Reichert-Meißl number for genuine butter varies from 17—32, although the majority of butters give figures varying from 23—26. The variation is due to the condition of the cows and to the quality of the food.

L. DE K.



**Adulteration of Butter.** By THEODOR PFEIFFER (*Chem. Zeit.*, 1899, 23, 39—40).—A sample of absolutely pure butter gave, on analysis, a Reichert-Meissl number of only 19.4, and a Koetstorfer number as high as 219.4. It would therefore have been liable to be reported as adulterated with a considerable amount of margarine. It was made from the milk of three cows fed on the usual mixed diet.

L. DE K.

**Butter Analysis.** By ALEXANDER ZEGA (*Chem. Zeit.*, 1899, 23, 312).—Butter is melted and filtered, and some of the fat is put into a test-tube and heated for 2 minutes in the boiling water-bath. One c.c. is drawn off with a small pipette previously heated and put into a glass-stoppered cylinder containing 20 c.c. of a mixture of 6 parts of ether, 4 parts of alcohol, and 1 part of glacial acetic acid. The cylinder is placed in water at 15—18°, when, if the sample is pure, the liquid remains clear or only deposits an inappreciable amount of fatty matter. With butter containing 10 per cent. or more of margarine, however, a more or less abundant deposit is obtained which may be examined microscopically. Drawings are given showing the considerable differences in appearance between the deposits from butter and from margarine. The process is also serviceable for the detection of tallow in lard; drawings of deposits from lard and tallow being also given.

L. DE K.

**Butter Analysis.** By W. LAWRENCE GADD (*Chem. News*, 1899, 80, 113).—In the application of Reichert's test, the use of alcoholic potash that has been kept may lead to erroneous results which may be obviated by the use of solid potash in the following manner: about 2.5 grams of butter fat just at its melting point is treated in an 8 oz. flask with 20 c.c. of methylated spirit freshly distilled from caustic potash; about 1 gram of solid caustic potash is added, and the flask plunged into hot water. The saponification being complete, the alcohol is evaporated with the aid of a current of filtered air, the mass dissolved in hot water, acidified with sulphuric acid, and subjected to distillation, &c.

D. A. L.

**Halphen's Test for Cotton Seed Oil.** By PAUL SOLTSIEN (*Chem. Centr.*, 1899, i, 1049; from *Zeit. öffent. Chem.*, 5, 106—107).—Halphen's test for cotton seed oil (*Abstr.*, 1898, ii, 358) works well even without addition of amylic alcohol and sodium chloride. 10 grams of the sample of fat are mixed with 2 grams of a 1 per cent. solution of sulphur in carbon bisulphide and introduced into a test-tube which is closed with a cork through which passes a tube blown out to a bulb; the mixture is then heated for 15 minutes on a water-bath, and the colour compared with that of a known mixture of fat and cotton seed oil treated in like manner. The colour, which is very permanent, strongly resembles that of a solution of potassium dichromate.

The test is very useful, because age or rancidity of the fats do not impair it in the least, and it shows the presence of cotton seed oil, even if this has been previously heated to 200°. Lard, tallow, fats from cheese, sesamé oil, olive oil, rape oil, linseed oil, poppy oil, arachis oil, hazelnut oil, and cod-liver oil are not affected.

L. DE K.

**Presence of Chlorinated Organic Compounds and Absence of Sulphur Compounds in Cotton Seed Oil.** By P. N. RAIKOW (*Chem. Zeit.*, 1899, 23, 769—770 and 802).—Although cotton seed oil does not contain sulphur, it gives the phloroglucinol-vanillin test (this vol., ii, 52); this is due to the presence of chlorinated compounds, which, on burning, yield hydrogen chloride. By means of the tubular lamp previously described, the oil was burnt in a beaker placed on its side and the inner surface of the beaker was kept moistened with potassium hydroxide solution. Dupont's method (*Abstr.*, 1896, i, 409) has also been employed, but no sulphur could be detected. The chlorinated compound is not extracted by water, but is somewhat volatile in superheated steam.

Olive oil and walnut oil, although they give the phloroglucinol reaction, are free from both sulphur and chlorine (compare Fox and Riddick, *Chem. News*, 1895, 71, 296; also Dupont and Charabot, *Bull. Soc. Chim.*, 1896, [iii], 15, 341). The presence of chloro-derivatives in cotton seed oil may be made use of in determining whether this oil has been employed in adulterating other oils. J. J. S.

**"Vegetale" (Cotton-Stearin): Isolation of Cholesterol and Phytosterol from Fats.** By F. WIRTHLE (*Chem. Zeit.*, 1899, 23, 250).—"Vegetale" consists of crude cotton-stearin, and occurs as a yellow, semi-solid mass which, after being melted, does not readily solidify. Its iodine number is 89.24, and its saponification number 196.1. It gives the Bechi test in a very marked degree, and shows a refraction of  $63.3^{\circ}$  at  $25^{\circ}$ . By using Böhmer's process for the isolation of cholesterol and phytosterol, the latter may be readily detected, and mixed crystals of both these substances may be obtained from lard adulterated with only 10 per cent. of "vegetale." Böhmer's process gives satisfactory results even with very rancid fats, and it is only when the samples have been kept for many years under unfavourable conditions that no crystals can be obtained. Kreis's process for the isolation of cholesterol and phytosterol (this vol., ii, 343) requires 50 grams of fat, whilst Böhmer's test may be made with 25 grams only, so it possesses no decided advantages. L. DE K.

**Isolation of Cholesterol and Phytosterol from Fats.** By OTTO FOERSTER (*Chem. Zeit.*, 1899, 23, 188).—The author objects to the process recommended by Kreis and Wolf (this vol., ii, 343), as in the case of a sample of oil of mustard it only gave 0.03 gram of phytosterol, whilst in another experiment, conducted by the author's process (this vol., ii, 121), 0.6 gram was obtained. L. DE K.

**New Reactions of Sesamé Oil.** By FERDINAND BREINL (*Chem. Zeit.*, 1899, 23, 647).—The author states that, in place of testing for sesamé oil with hydrochloric acid and a 2 per cent. alcoholic solution of furfuraldehyde, a 3 per cent. alcoholic solution of hydroxybenzaldehyde, vanillin, or piperonal may, with advantage, be substituted. L. DE K.

**Bishop's Test for Sesamé Oil.** By HANS KREIS (*Chem. Zeit.*, 1899, 23, 802—803).—Stale sesamé oil, when shaken with an equal

volume of hydrochloric acid of sp. gr. 1.19, turns green, and if sugar is also added, a blue colour is developed.

A remarkable result was obtained by the author: a very rancid olive oil gave no colour with hydrochloric acid, but on adding some fresh sesamé oil, which also gave no test with hydrochloric acid, the green colour was at once apparent. Further results are promised.

L. DE K.

**Analysis of Human Urine.** By WILLIAM CAMERER and FRIEDRICH SÖLDNER (*Zeit. Biol.*, 1899, 38, 227—290).—The principal methods of urine analysis are criticised and experimentally compared. The most important outcome appears to be that, in the estimation of urea by the Mörner-Sjöquist method, part of the nitrogen of hippuric acid, allantoin, and creatinine is reckoned as urea nitrogen. The methods of estimating uric acid, alloxuric bases, ammonia, and other substances are also examined.

W. D. H.

[Estimation of Allylthiocarbimide in] Seeds of some Varieties of Brassica and Sinapis. By WILHELM KINZEL (*Landw. Versuchs-Stat.*, 1899, 52, 169—193).—The method employed was that of Direk as modified by Schlicht (Abstr., 1892, 1035), except that the substance was steam-distilled, as proposed by Förster (*Landw. Versuchs-Stat.*, 1898, 50, 419). Powdered rape cake (15 grams) and white mustard (4 grams) are mixed with water (150 c.c.) and tartaric acid (0.25 gram) in a 500 c.c. Erlenmeyer flask. The heating of the steam flask is so arranged that steam begins to pass over in about half-an-hour; the Erlenmeyer flask is now heated with a small flame until, in  $1\frac{1}{2}$  hours, 200 c.c. has distilled over. The vapours pass through a 0.6 cm. tube, 70 cm. long, into three receivers (an Erlenmeyer flask, a Will-Varrentrapp apparatus, and a second Erlenmeyer flask) containing 100, 18, and 10 c.c. respectively of alkaline permanganate solution. As the distillation proceeds, the heating of both flasks must be increased to avoid violent rising of the liquid in the Will-Varrentrapp apparatus. The safety tube of the steam flask is only opened in the case of the permanganate flowing backwards to the flask containing the substance. The liquid in the three receivers is mixed, heated for an hour on a water-bath, and after cooling to 70°, treated with alcohol (25 c.c.) and diluted to 501 c.c. Every 3.333 grams of precipitate ( $\text{KH}_3\text{Mn}_4\text{O}_{10}$ ) corresponds with 1.012 c.c. of solution at 17.5°. After filtration and addition of a little acid and iodine, the sulphuric acid is determined in the manner described by Schlicht (*loc. cit.*), the result being corrected by adding 0.00319 to the amount of barium sulphate from 400 c.c.

The results obtained with a number of samples of different varieties of brassica from India are given.

N. H. J. M.

**Estimation of Urea.** By SERGEI SALASKIN and J. ZALESKI (*Zeit. physiol. Chem.*, 1899, 28, 73—87).—The estimation of urea in urine by the Mörner-Sjöquist method gives results which are too high. This is because part of the hippuric acid nitrogen is reckoned as urea nitrogen; and the more hippuric acid the urine contains the greater the error. The method suggested is to heat the residue after the ether

and alcohol are evaporated off, in a glass tube, and to estimate the urea from the ammonia thus given off.

W. D. H.

**Volumetric Estimation of Aniline and Bromine.** By GEORGES DENIGÈS (*J. Pharm.*, 1899, [vi], 10, 63—66).—A claim for priority with respect to the method proposed by François (this vol., ii, 713) for the estimation of aniline.

H. R. LE S.

**Methods of Estimating Alkaloids.** By OTTO LINDE (*Arch. Pharm.*, 1899, 237, 392—408. Compare this vol., ii, 534).—Keller's method (compare Abstr., 1897, ii, 84) is open to the following objections. (1.) The assumption is made that the solvent either extracts all the alkaloid, or, at least, contains it in equal concentration throughout, whether within or without the drug; it is found, however, that the residual part, including the much-swollen drug, contains proportionally more alkaloid. (2.) The amount of solution removed is assumed to contain 100/120 of the alkaloid; as a matter of fact, the total amount of the solution may have suffered an increase owing to the solution in it of fat, and even of soap. (3.) The repeated shaking and the large amount of solvent used are objectionable; shaking once with a smaller quantity suffices if the volume of the aqueous solution is kept relatively small; it may also be saturated with some salt. (4.) It is better to measure the quantities of solvent used than to weigh them; pipettes graduated for use with water may be employed.

Ekroos' method (this vol., ii, 74) cannot be used with drugs from which ammonia or an aliphatic amine is liberated by treatment with soda; neither can it be used with drugs which contain oil, as in these cases a soap is formed which dissolves in the chloroform-ether, and uses up some of the sulphuric acid.

Katz's method (Abstr., 1898, ii, 547) is equally unavailable for drugs from which soda liberates ammonia or an amine.

It is better not to estimate an alkaloid only by titrating its solution, but first to weigh it after evaporation of the solution, in which process volatile alkalis are removed, and then to titrate the residue; a serious discrepancy between the two results would indicate adulteration.

C. F. B.

**Hydrastine Pentiodide Hydriodide.** Volumetric Estimation of Hydrastine and Berberine in the Root of *Hydrastis Canadensis*. By HARRY MANN GORDIN and ALBERT B. PRESCOTT (*Arch. Pharm.*, 1899, 237, 439—446).—When a dilute solution of hydrastine is added to a large excess of a solution of iodine in aqueous potassium iodide, a dark brown compound,  $C_{21}H_{21}O_6N, HI, I_5$ , is precipitated; this melts readily under water; it loses 5I when treated with sulphurous acid or sodium thiosulphate.

For the estimation of the alkaloids in *Hydrastis canadensis*, 10 grams of the powdered root are stirred into a paste with a mixture of alcohol, concentrated ammonia, and ether (1 : 1 : 6 parts by volume), and allowed to remain in a well-closed vessel for several hours. The mixture is then dried, at first in a good draught and then over sulphuric acid under diminished pressure; the residue is transferred to a Soxhlet apparatus, being rinsed out with powdered barium nitrate, and the hydrastine is

extracted completely with absolute ether; the ether is evaporated from the extract, and the residue dissolved in acidified water, and the solution diluted to 100 c.c. In a graduated 100 c.c. flask, 20—30 c.c. of a standard iodine solution (of about 1 per cent. strength) are placed, 20 c.c. of the filtered hydrastine solution run in, and the mixture diluted to the mark and shaken until the pentiodide has all separated; the mixture is then filtered, and the excess of iodine determined by titrating 50 c.c. of the filtrate with standard sodium thiosulphate solution. Every 1 part of iodine used corresponds with 0.60403 part of hydrastine. Or the alkaloid may be estimated gravimetrically by shaking 20 c.c. of the filtered hydrastine solution with benzene and ammonia, removing the alkaloid from the benzene solution by shaking with acidified water, and then from the acid solution with ammonia and ether, the ethereal solution is finally evaporated in a dark place at the ordinary temperature, and the residue of hydrastine weighed.

The residue in the Soxhlet apparatus contains the berberine, which is not soluble in absolute ether; it is dried by passing a current of dry air through the apparatus, and is then extracted with alcohol. The alcohol is removed from the extract by heating it with 200 c.c. of water on the water-bath; the residual liquid is acidified with acetic acid, cooled, and filtered into a conical flask; in this it is shaken for 10—15 minutes with 6—8 c.c. of acetone and enough 10 per cent. caustic soda solution to render the reaction alkaline, and set aside for 2—3 hours. The precipitated acetone compound is washed, and warmed in the same flask with 200—300 c.c. of very dilute sulphuric acid until it has all dissolved, the solution is poured into a long-necked Kjeldahl flask and boiled for  $1\frac{1}{2}$ —2 hours; when cold, it is added to 100 c.c. of *N*/20 potassium iodide solution contained in a graduated 1000 c.c. flask, diluted to the mark, shaken, and left overnight. Then 500 c.c. are filtered from the precipitate of berberine hydriodide into another 1000 c.c. flask, treated with 50 c.c. *N*/20 silver nitrate and nitric acid, diluted to the mark, and filtered; the excess of silver is determined by titrating 500 c.c. of the filtrate with *N*/40 ammonium thiocyanate. The number of c.c. of the iodide solution used, multiplied by 0.167125, gives the percentage of berberine in the root. C. F. B.

**Vitali's Test for Veratrine.** By IWAN L. KONDAKOFF (*Chem. Zeit.*, 1899, 23, 4).—The author confirms Kunz-Krause's statement that when veratrine is evaporated with fuming nitric acid and the residue treated with alcoholic potash, the mixture turns blood-red and evolves a strong odour of coniine. The odorous substance is really coniine, and not  $\beta$ -picoline. L. DE K.

**Melzer's Picrotoxin Reaction.** By HANS KREIS (*Chem. Zeit.*, 1899, 23, 21—22).—The author warns toxicologists that cholesterol and phytosterol also give reactions with benzaldehyde and sulphuric acid very similar to that described as characteristic for picrotoxin by Melzer (*Abstr.*, 1898, ii, 650). L. DE K.

**Estimation of Proteids in Blood Serum.** By GUSTAVE PATEIN (*J. Pharm.*, 1899, [vi], 10, 244—249).—*Alkaliseralbumin* is the name given by the author to the albumin precipitated by acidifying diluted

human blood serum with 10 per cent. acetic acid. For its estimation, 100 c.c. of the serum are diluted with 900 c.c. of water, and the liquid is rendered faintly acid with 10 per cent. acetic acid. The mixture is left for 24 hours, and the precipitate washed by decantation with water slightly acidified with acetic acid. It is then dissolved in 60 c.c. of water previously acidified with acetic acid, 1 to 2 grams of sodium sulphate or chloride are added, and the solution boiled. From this stage, the process is the same as for the estimation of albumin.

*Estimation of total albumin.*—10 c.c. of the serum are diluted to 100 c.c. with water, the liquid is rendered very faintly acid with acetic acid, and 2 grams of sodium sulphate are added. The mixture is boiled, and the precipitate, collected on a tared filter, washed with boiling water, alcohol, and ether, and dried and weighed.

*Estimation of serin and serum-globulin.*—The serum previously diluted with 9 times its volume of water, is rendered faintly acid with acetic acid and the mixture left for 24 hours. It is then heated to boiling, and the precipitate collected, dried, and weighed.

*Estimation of serin.*—The serum is diluted with 9 times its volume of water, and 100 c.c. of this solution are saturated with magnesium sulphate. The liquid is filtered, and an aliquot part of the filtrate, faintly acidified with acetic acid, is boiled, and the precipitated serin dried and weighed. The serum-globulin is estimated by difference. 1000 grams of blood serum were found to contain : total proteids, 75.4 ; alkaliseralbumin, 2.45 ; serin and other proteids, 45.03 ; and globulin, 27.92.

H. R. LE S.

**Estimation of Albumin in Urine.** By GEORGES DENIGÈS (*J. Pharm.*, 1899, [vi], 10, 97—102).—The author's method for the estimation of casein in milk (*Abstr.*, 1897, ii, 532) is applicable to the estimation of albumin in urine. For urine containing not more than 1.1 grams of albumin per litre, the method is as follows: 20 c.c. of mercuric potassium iodide and 2 c.c. of glacial acetic acid are added to 150 c.c. of the urine, and the whole diluted to 200 c.c. The mixture is filtered, and 25 c.c. of an ammoniacal solution of potassium cyanide (equivalent to  $N/20$  silver nitrate) are added to 125 c.c. of the filtrate, the whole left for 2 or 3 minutes, and again filtered. To 120 c.c. of the last filtrate,  $N/10$  silver nitrate is added until a faint, but permanent, opalescence is produced. The number of tenths of a c.c. of silver nitrate less 48 (a constant) gives the number of decigrams of albumin in a litre of urine.

If the urine contains more than 1.1 grams of albumin in a litre, then the number of c.c. of urine used must be such that it shall not contain more than 0.15—0.16 gram of albumin, and shall be a simple ratio of 150. If the urine contains less than 0.2 gram of albumin in a litre, the amount is determined by comparing the opalescence produced by the addition of 2 c.c. of a 5 per cent. solution of sodium metaphosphate and 4 drops of sulphuric acid to 10 c.c. of the urine and heating in boiling water for 5 minutes, with that produced, under the same conditions, with urine solutions containing a known weight of albumin.

H. R. LE S.

## ERRATA.

## VOL. LXX. (ABSTR., 1896).

## PART I.

Page	Line	
446	8* and 3*	for "sobreritritol" read "sobrerythritol."

## VOL. LXXII. (ABSTR., 1897).

## PART II.

37	18*	for "1895" read "1896."
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## VOL. LXXIV. (ABSTR., 1898).

## PART I.

Page	Line	
53	25	for "Dobie" read "Dobbie."
700	4*	„ "α-uric" read "α-methyluric."

## PART II.

14	2* and 1*	for " $C_5H_6$ " read " $C_6H_5$ ."
277	5*	„ " $HNO_3, 10H_2O$ " read " $10HNO_3, H_2O$ ."

## INDEX.

Page	Col.	Line	
709	ii	35	for "H. M. Goodwin" read "Harry Mann Gordin."
713	ii	5*	should read "Salvadori, Roberto. See Raffaele Nasini."
718	i	10*	for "21" read "213."
900	ii	13	„ "1889" read "1898."
935	i	22	„ "diphenylethylene" read "phenylethylene."

## VOL. LXXVI. (ABSTR., 1899).

## PART I.

Page	Line	
2	2	for "sodium" read "iodine."
42	13, 14, and 19, in formulæ,	for " $\cdot CHCl_3$ " read " $\cdot CH(CCl_3)$ ."
48	bottom	„ „ " $\cdot CO \cdot NH$ " „ " $\cdot CO \cdot NH_2$ "
53	22*	for "Rizzo Niccolò" read "Niccolò Rizzo."
98	20	„ "ethylene" read "ethane."
108	16	„ "foregoing" read "following."
124	3	„ "1-amido-" read "2-amido-."
126	3*	„ "diphenylthiocarbamate" read "diphenylcarbamate."
144	3	„ " $C_{22}H_{18}N_2O$ " read " $C_{22}H_{18}N_2O_2$ ."
185	8*	„ "37" read "371."
197	12	„ " $CPhFCl_2$ " read " $CPhF_2Cl$ ."
203	11	„ " $[Me : N_2 : NO_2]$ " etc., read " $[Me_2 : N : NO_2]$ " etc.
256	top	„ "dimethylacetonecyanhydrin" read "acetonecyanhydrin."
„	25	should read "is converted into monochlorisobutylacetonitrile or α-chlorocapronitrile."
„	13*	for "α-chlorocapronitrile" read "α-chlorocaprylonitrile."

\* From bottom.

Page	Line	
258	top	for " $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COCl}$ " read " $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COCl}$ ."
268	13*	„ "sulphuric" read "nitric."
278	5	„ " $\alpha$ -bromisobutyrylmetaxylylidide" read " $\alpha$ -bromisovalerylmetaxylylidide."
288	1	„ " $\alpha$ -metamethoxyglyoxylic" read " $\alpha$ -metamethoxyphenylglyoxylic."
„	21 and bottom	„ " $\text{CO}\cdot\text{COOEt}$ " read " $\text{CO}\cdot\text{COOH}$ ."
360	8*, 11*, and 15*	for "4" read "4."
387	2	for "indigotin" read "indican."
427	20	„ "Abstr., 1899," read "Abstr., 1898."
489	21*	before " $\alpha$ -acetaldehydedisulphonate" insert "brom."
498	20	for " $(\text{CH}_2\text{Et})$ " read " $(\text{CH}_2\text{Ph})$ ."
512	17	„ " $\text{C}_{10}\text{H}_9\text{N}_4\text{O}$ " read " $\text{C}_{10}\text{H}_9\text{NO}_4$ ."
537	25	„ "strychnine" read "quinine."
564	6, 7, and 8	„ "-phosphinic" read "-phosphinous."
664	14*	„ "benzenesulphonic chloride (2 mols.) on ethylenediamine (1 mol.) in presence of an excess of," read "trimethylene bromide on ethylenedibenzosulphonamide dissolved in."
„	9*	„ " $\text{C}_9\text{H}_5$ ," read " $\text{C}_9\text{H}_4$ ."
696	16	„ " $\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ " read " $\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ ."
726	27	„ " $\text{C}_5\text{H}_9\text{Cl}\cdot\text{OH}$ " read " $\text{C}_5\text{H}_9\text{ClO}_2$ ."
736	19*	„ "ethylic" read "amylic."
749	5* and 2*	„ " $\cdot\text{NC}_3\text{H}_6$ " read " $\cdot\text{NC}_2\text{H}_4$ ."
761	5	„ " $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NHBz})\cdot\text{CH}\cdot\text{COOH}$ " read " $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{C}(\text{NHBz})\cdot\text{COOH}$ ."
766	12*	„ "(methane-1 : 2 : 6 : 8-tetrol)" read "(menthane-1 : 2 : 6 : 8-tetrol)."
798	3*	„ "Phenylfurfurylamine" read "Phenylfurfurylcarbinyllamine."
814	3	„ "phenylglutarate" read "phenylglutarocarboxylate."
848	10*	„ " $\text{C}_2\text{H}_4(\text{CH}\cdot\text{CHMe})$ " read " $\text{C}_2\text{H}_4(\text{CH}\cdot\text{CHMe})_2$ ."
875	20*	„ "propylic" read "isopropylic."
887	5*	„ " $\text{NHPh}\cdot\text{CO}\cdot\text{NH}_2\text{R}$ " read " $\text{NHPh}\cdot\text{CO}\cdot\text{NHR}$ ."
891	21	„ "-3-dinitro-" read "-3 : $\omega$ -dinitro-."
917	8*	„ " $\alpha$ -Dinaphthylbenzene" read " $\alpha$ -Dinaphthylbenzidine."

## PART II.

5	16*	„ "1897, 28," read "1898, 27."
8	18*	„ "saumontite" read "laumontite."
11	18	„ "SEIDENSTRAKER" read "SEIDENSTICKER."
102	10	„ " $\text{Ph}_3$ " read " $\text{PH}_3$ ."
140	bottom	„ " $\text{CdC}_2\text{O}$ " read " $\text{CdC}_2\text{O}_4$ ."
159	„	„ " $\text{WO}_2$ " read " $\text{WO}_3$ ."
278	11*	„ "YORRE" read "JORRE."
290	19	„ "1895" read "1896."
355	24	„ "atoms" read "equivalents."
396	10	„ "has" read "is."
401	15	„ "148 Cal." read "14.8 Cal."
„	17	„ "43 Cal." read "4.3 Cal."
„	18	„ "-60 Cal." read "-6.0 Cal."
„	19	„ "-17 Cal." read "-1.7 Cal."
434	2*	„ "optically active" read "optically birefringent."
436	3* and 7*	„ "Tachylite" read "Tachylite."
483	25	„ "nitrate" read "nitrite."
503	21*	„ "Fats" read "Fate."
545	9 and 14	„ "nitrogen" read "nitric oxide."
684	18*	„ "acres" read "ares."
725	22	„ " $\text{Cd} \mid \text{CdCl}_2 \mid \text{Cl}_2$ " read " $\text{Cd} \mid \text{CdCl}_2 \mid \text{Cl}$ ."
762	14	„ "JÓZSEF" read "JÓZEF."

\* From bottom.



## INDEX.

Page	Col.	Line	
1005	i	32*	} for "YORRE" read "JORRE."
1043	i	27*	

## COLLECTIVE INDEX (1883—1892).

**Japp, Francis Robert, and Edward Cleminshaw**, "constitution of glycocine," should be "glycosine."

"**Glucosine**, constitution of" (JAPP and CLEMINSHAW), should be "**Glycosine**."

"**Tetraphenylglycocine**" should be "**Tetraphenylglycosine**."

\* From bottom.